Biorenewable Resources

Engineering New Products from Agriculture

SECOND EDITION

Robert C. Brown and Tristan R. Brown

WILEY Blackwell

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Second Edition

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Preface

Biorenewable Resources was originally published in 2003 as a textbook to support a new interdisciplinary graduate program in Biorenewable Resources and Technology at Iowa State University. This was two years before the passage of the Energy Policy Act of 2005 launched the biofuels boom in the United States. At the time there was relatively little current scientific literature to support the preparation of the book due to many of the sources dating back a decade or more. The field has grown tremendously since then, encouraging the publication of a second edition of *Biorenewable Resources*.

As with the first edition, the second edition is intended as a text for upper level undergraduate students and first year graduate students in science and engineering who are seeking a broad perspective of the emerging field of biorenewable resources. Traditional academic disciplines are organized to provide students in-depth training and intellectual focus in a single field such as agriculture, chemistry, engineering, environmental science, or economics. *Biorenewable Resources* brings together these disciplines to provide students with an appropriate system perspective valued by prospective employers and those seeking to work in this field.

The thirteen chapters of this book do not assume any previous training in biorenewable resources, although most students should have undergraduate training in science or engineering. Chapter 1 is an introduction to the field of biorenewable resources, which includes a brief history of the use of biorenewable resources and a description of the motivations for advancing the biobased products industry. Chapters 2 and 3 provide fundamental concepts of engineering thermodynamics and organic chemistry important to understanding bioenergy and biobased products. These two chapters are aimed at students who may have deficiencies in these concepts or who desire a review of the topics. The chapter on engineering thermodynamics includes expanded descriptions of mass and molar balances applied to conversion, yield, and selectivity of chemical reactions. It also includes discussions on energy return on energy invested and the role of exothermic versus endothermic reactions in the manufacture of energy products. Chemical equilibrium receives more extensive treatment than in the first edition. The chapter on organic chemistry includes descriptions of anhydrosugars, important in thermochemical conversion of carbohydrate-rich biomass, and lignin chemical composition.

Chapter 4 is a description of biorenewable resources. This chapter includes sections that defines the resource base, categorizes the different kinds of biorenewable resources, including both waste materials and dedicated energy crops, describes properties that are important to the handling and processing of biorenewable resources, provides information on yields of various kinds of biomass, and assesses the availability of different kinds of biorenewable resources. The second edition includes extensive coverage of oleaginous (lipid-rich) biomass such as microalgae. Chapter 5 is an introduction to production of biorenewable resources. In addition to descriptions of growing and harvesting herbaceous energy crops and short rotation woody crops, the second edition describes cultivation and recovery of microalgae, considered a promising aquatic species for production of biofuels and biobased products. This chapter also includes descriptions of storage systems and the prospects for using transgenic crops in production of biorenewable resources. Chapter 6 is an introduction to the wide array of bioenergy and biobased products that are currently produced or anticipated from biorenewable resources. Major topics in this chapter include process heat, biopower, biofuels, commodity chemicals, synthetic biopolymers (new to the second edition), and natural fibers.

The next four chapters are devoted to the processes by which biorenewable resources are transformed into bioenergy and biobased products. Chapter 7 focuses on biochemical conversion of carbohydrate-rich feedstocks to ethanol and other products, including hydrocarbons (new to the second edition). Chapter 8 describes thermochemical conversion of lignocellulosic biomass. The second edition expands coverage of gasification technology to include syngas cleaning and catalytic upgrading to fuels and chemicals. Considering the increasing interest in pyrolysis as a pathway to biofuels, this topic has been expanded to include fundamentals of pyrolysis, different kinds of pyrolysis processes and equipment, and catalytic upgrading of bio-oil to biofuels. Solvolysis has been added as an alternative approach to producing bio-oil or sugars. Chapter 9 considers both biochemical and thermochemical processes for the conversion of oleaginous biomass into fuels and other products. Chapter 10 explains how natural fibers can be separated from biorenewable resources for use in the manufacture of paper and building materials.

The final three chapters deal with environmental, economic, and policy issues. Chapter 11 describes the environmental impact of producing and processing biorenewable resources and using the resulting products. Extensive discussion of land use change (both direct and indirect) associated with production of biofuels is included in the new edition. Chapter 11 also describes environmental concerns associated with the use of transgenic crops as biorenewable resources. Chapter 12, an introduction to the economics of biorenewable resources, has been extensively updated to reflect current methodologies in technoeconomic analysis of biorenewables. The chapter includes separate discussions on estimating the costs of producing crops and manufacturing biobased products. The chapter concludes with specific cost estimates for various biobased products. Chapter 13, new to the

second edition, explores the role of government policy in promoting the adoption of biofuels as an alternative to fossil fuels and imported petroleum. The chapter describes the various policies employed by governments around the world to promote bioenergy.

Although many colleagues influenced the preparation of the first and second edition, we would like to especially acknowledge the assistance of Kaige Wang in reviewing some of the chapters; Chris Deal in researching the biorenewable resources described in Appendix A; Trevor Brown for preparing the illustrations new to this edition; Carolyn Brown in assisting with indexing; and Justin Jeffryes and Stephanie Dollan at Wiley for providing assistance and encouragement in preparing the second edition. Of course, errors and omissions are solely the responsibility of the authors. We would also like to thank our wives, Carolyn and Kate, for tolerating this father-son collaboration, which cut into much "free time" during the last year.

Robert C. Brown and Tristan R. Brown
Ames, IA
October 2013

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CHAPTER
1

Introduction

1.1 Transitions

Mankind has gone outside the biotic (i.e., derived from living organisms) environment for the majority of its material needs only recently. Plant-based resources were the predominant source of energy, organic chemicals, and fibers in the West as recently as 150 years ago, and they continue to play important roles in many emerging economies. The transition to non-biological sources of energy and materials was relatively swift and recent in the history of the world. Many assumed that the transition was irreversible. Indeed, in the 1960s it appeared that fossil fuels were only a short bridge to the nuclear age, with fission reactors supplying energy for power and transportation fuels in the waning decades of the twentieth century, while fusion reactors would ultimately provide limitless supplies of energy. In this scenario, petroleum and natural gas would continue as the source of building blocks for organic chemical synthesis.

Reality has proved more complicated, uncertain, and unsettling. In many parts of the world, nuclear fission has not lived up to its promise and has become a political pariah in the face of reactor safety concerns and unresolved questions about radioactive waste disposal. Nuclear fusion has a lively history of tokamaks, inertial confinement, and cold fusion, but no breakeven in energy output. Petroleum continues to supply most of the world's demand for transportation fuels and commodity chemicals but the remaining reserves are increasingly concentrated in the hands of a few capricious nations. Coal is plentiful but introduces tremendous burdens on the environment, ranging from acid rain to mercury poisoning. Concerns about global climate change due to carbon dioxide emissions raise questions about the future use of all fossil fuels. In this political and social climate, there are calls for the development of reliable and long-term resources that have fewer areas of environmental impact than fossil resources. This book explores a return to the biotic environment for energy, chemicals, fuels, and fibers.

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1.2 Definitions

Biorenewable resources, also known as biomass, are organic materials of recent biological origin. Biomass is obtained from the thin region near the surface of the Earth known as the *biosphere* that supports living organisms. Biomass may be grown as crops, but the vast majority of the world's biorenewable resources are forests, prairies, marshes, and ocean biomes. The energy to build the chemical bonds of these organic materials comes mostly from sunlight. Solar energy collected by photosynthetic organisms is converted into energetic chemical bonds to produce proteins, oils, and carbohydrates. This stored chemical energy is raw material that can be used as a resource of renewable carbon and energy for the production of bioenergy and biobased products. In contrast, coal, oil, and natural gas are thought to be derived from microorganisms and plants buried and transformed into fossil fuels eons ago. In this view, the only difference between biomass and fossil fuels is the degree that nature processes biogenic materials.[1]

Biorenewable resources, by definition, are sustainable natural resources. Sustainable implies that the resource renews itself at such a rate that it will be available for use by future generations. Thus, a stand of grass cut every year for a hay crop represents a biorenewable resource, while a field cleared in a tropical rainforest for "slash and burn" agriculture is not.

Human societies, like living organisms, require sources of energy and carbon to survive and grow. Most living organisms obtain energy and carbon from the biosphere. In contrast, most modern human societies rely on fossil resources for energy and carbon, although this is a relatively recent historical development. Before wide-scale exploitation of fossil resources starting in the eighteenth century, human societies were almost completely dependent on biorenewable resources. The challenge of the twenty-first century is to create a *bioeconomy*, in which human societies obtain sustainable sources of energy and carbon from the biosphere.

Energy from biorenewable resources is used to produce *bioenergy*. Carbon from biorenewable resources is used to produce *biobased products*. Of course, bioenergy is based on fuels that contain carbon and biobased products contain chemical energy in their carbon bonds, but it is useful to distinguish between these two kinds of products from biorenewable resources as either sustainable sources of energy or carbon.

Bioenergy includes process heat, biopower, and biofuels. *Process heat* is often thought of thermal energy for industrial processing, but it also includes energy used for residential and commercial thermal energy demand such as space and water heating.

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[1] For a fascinating presentation of an abiogenic hypothesis on the origin of fossil fuels, see Thomas Gold's *The Deep Hot Biosphere*.

Biopower is the conversion of biorenewable resources into electrical power. When power generation is based on heat engines, the chemical energy of biorenewable resources is first converted into thermal energy before conversion into power. When power generation is based on electrochemical fuel cells, the chemical energy of biorenewable resources is first converted into hydrogen before conversion to power.

Biofuels are chemicals derived from biorenewable resources that have sufficient volumetric energy densities (enthalpies of reaction per unit volume) and combustion characteristics to make them suitable as transportation fuels. Most biofuels are liquids such as ethanol or green diesel, but compressed gases have also been proposed and evaluated for use in vehicular propulsion. It should be kept in mind that another way to use biorenewable resources for transportation is to convert it to biopower and store the electricity in vehicular batteries—electric cars.

Biobased products include chemicals and materials. *Biobased chemicals* include fine chemicals like pharmaceuticals and nutraceuticals, but the emphasis is on high-volume commodity chemicals. *Biobased materials* can be thought of as finished products manufactured from biorenewable resources. Most prominent in this category are *biobased fibers*, including both *natural fibers* and *synthetic fibers*. *Natural plant fibers* are bundles of long, thin plant cells with durable walls of lignocellulose (animal fibers are also natural fibers but are not treated in this book). *Synthetic fibers* are spun from synthetic polymers, manufactured from chemical building blocks known as monomers. Petroleum is the source of the vast majority of monomers and hence synthetic fibers, but synthetic fibers can also be manufactured from monomers derived from biorenewable resources.

1.3 Brief History of Biorenewable Resource Utilization

Many of the advances in early human society were based on the exploitation of biorenewable resources. The first campfire, dating to as early as 500 000 years before the present (BP), was most surely kindled from wood rather than coal. Evidence that vegetable oils and animal fats were sources of illumination by 40 000 years BP is found at Upper Paleolithic cave sites in Europe. Draft animals represented mankind's first use of prime movers other than their own muscle power. Grasses and cultivated grains, fed to draft animals, provided power and transportation needs in early societies.

Except for stone tools, virtually all possessions until the advent of the Bronze Age were biobased products. Wood was a versatile composite material for the construction of hunting and farming implements. Cotton fibers were spun and twined in Peru as long ago as 12 000 years BP. Fermentation of sugars to ethanol was mastered as long ago as 6000 BP, but the product remained too precious for any but convivial purposes for thousands of years afterward.

Wood remained the primary fuel for most pre-twentieth-century societies, although there are traditions of using grass for steel making in Africa and "lightly processed" grass in the form of dried buffalo dung for cooking fires in the American West. The preeminence of bioenergy began to wane when the great forests of the Northern Hemisphere were depleted by the voracious fuel demand in the manufacture of copper, iron, and glass and the powering of steam engines. By the mid-eighteenth century, coal had supplanted wood as the primary energy source for European and North American countries.

Biorenewable resources continued to be important as sources of chemicals and materials for another 75 years aided by advances in industrial chemistry. Gum turpentine, rosins, and pitches, collectively known as naval stores, were extracted from coniferous trees for maintaining wooden ships and ropes. Natural latex from the hevea rubber tree was vulcanized to an elastic, waterproof material used in numerous consumer products. The "destructive distillation" of wood yielded methanol (wood alcohol) and other industrially important compounds. Wood pulping was developed to separate cellulose fibers used in paper and cardboard products. From cellulose came the first semi-synthetic plastic, celluloid. Advances in the brewery industry eventually led to commercial fermentation of a variety of organic alcohols and acids with applications far beyond the beverage industry.

With the exceptions of lumber production for building materials, fiber production (wood pulping and cloth manufacture), and ethanol fermentation, the manufacture of biobased products rapidly declined in the twentieth century. This decline was not the result of resource scarcity, as was the case for bioenergy. Instead, rapid advances in the chemistry of coal-derived compounds during the late nineteenth century followed by the development of the petrochemical industry in the early twentieth century provided less expensive and more easily manipulated feedstock for the production of chemicals and materials.

1.4 Motivation for Returning to a Bioeconomy

Despite gradually rising prices for fossil fuels since that time, economics currently do not favor bioenergy and biobased products. However, other factors are coming into play that increases the attractiveness of biorenewable resource utilization. These factors include desires to improve *environmental quality*, concerns that *national security* is compromised by overreliance on foreign sources of fossil fuels, the presence of *excess agricultural production* capacity in many developed nations, and the importance of *rural development* in improving economies of many agricultural regions.

1.4.1 Environmental Quality

The production and utilization of fossil fuels introduce several environmental burdens of increasing concern. These burdens have *local*, *regional*, and *global impacts*.

Production includes mining for coal and drilling for petroleum and natural gas. Most of the impacts are local in nature. Mining leaves behind spoil piles and acid drainage. Drilling can result in oil spills or sites contaminated by drilling mud or brackish water.

Utilization of fossil fuels can yield a plethora of local, regional, and environmental impacts. *Local impacts* can arise from solid waste disposal sites for ash from coal combustion or coke or sulfur from petroleum refineries. Combustion of coal or petroleum-based motor fuel also produces carbon monoxide, fine particulate matter, and smog as local pollution problems. *Regional impacts* of fossil energy utilization are mostly the result of acid rain, which is generated from sulfur dioxide and nitrogen oxides released during combustion. Acid rain can affect environments half a continent away from the point of pollutant emission. *Global impacts* are of two kinds: ozone depletion in the stratosphere and global climate change. Ozone depletion is usually associated with the release of chlorofluorocarbons from refrigeration equipment and aerosol cans. Nitrogen oxides have also been implicated in upper atmosphere reactions that destroy ozone molecules. However, the greatest concern with regard to global impact is the possible role of carbon dioxide released during combustion in contributing to the greenhouse effect in the atmosphere. Although the magnitude of this problem is still being assessed, there have been calls to greatly reduce the net rate of emission of carbon dioxide from the use of fossil fuels.

Bioenergy and biobased products are not a panacea for these problems. However, the environmental burden from the use of biorenewable resources is generally much less than from the use of fossil resources. An exact accounting of the benefits of using biorenewable resources is a difficult and sometimes politically charged process. For example, some argue that the benefits of using a 10% blend of ethanol in gasoline to reduce carbon monoxide emissions from spark-ignition engines are outweighed by the increased volatility of this fuel blend, which increases the release of unburned hydrocarbons to the atmosphere, a factor in smog formation.

1.4.2 National Security

In 1974, a severe economic crisis developed in many parts of the world as a result of disruptions in the distribution of petroleum to markets. The so-called *energy crisis* was commonly ascribed to dwindling reserves of petroleum resources, and many experts predicted that looming energy scarcity would drive petroleum prices from a few dollars per barrel to over $100, plunging the world into an economic depression that would be difficult to reverse. These concerns provided the impetus for a short-lived effort in the United States to commercially implement alternative energy sources, including solar, wind, biomass, and coal, to provide future energy. However, by 1980 petroleum prices had considerably moderated, and it was understood that an actual shortage of energy had never existed. Instead, a decision by Arab nations to boycott the sale of petroleum to the United States was responsible for temporary escalations in the world price of oil. The boycott

was an effort to influence US foreign policy in the Middle East, which favored the state of Israel in its conflicts with surrounding Arab states. Although disruptive in the short term, ultimately the boycott and various production quotas were lifted and the world price for petroleum dropped. This threat to national security failed because the United States and other nations responded by reducing their dependence on foreign sources of oil through energy conservation and energy efficiency improvements and by switching to domestic energy sources, mostly coal, natural gas, and petroleum. As demand for Middle Eastern petroleum dropped, these countries saw the major source of their revenues evaporating; economic survival forced them to suspend their efforts to use "the oil weapon," as it was called.

The lesson is that effective national security incorporates an energy policy that reduces heavy reliance on foreign cartels for energy resources. However, there is some evidence that this lesson is not being heeded in the United States, where dependence on petroleum imports now exceeds that of 1974. As a percentage of petroleum demand, the role of imported petroleum into the United States exceeded 50% in 2001 and is expected to fall only slightly to 48% by 2020. With two-thirds of world petroleum reserves located in the Middle East (including the Caspian basin), increased dependence is inevitable unless domestic energy sources such as biorenewable resources are developed.

1.4.3 Excess Agricultural Production

A frequently expressed concern about shifting agriculture toward production of biobased products is the potential impact on food production. Securing a safe and inexpensive food supply is the keystone of agricultural policy in the United States. Many people oppose the use of agricultural lands for the production of bioenergy and biobased products on the grounds that, at best, domestic food prices will rise and, at worse, starvation will increase in developing countries that are dependent on agricultural imports.

In fact, agricultural production in excess of domestic use and export demands exists in the United States as well as in a growing number of other countries. The United States in 1990, with a population of 250 million people, had 12% less land in agricultural production than it did in 1929, when the population was only 120 million. The reason for this decline in agricultural lands is primarily due to increasing crop productivity. For example, US corn yields between 1929 and 1990 increased from 22–30 bushels per acre to 101–139 bushels per acre. These improvements are the result of advances in plant genetics, fertilizers, pesticides, and production practices. In an effort to keep production in balance with demand, the US government encouraged development of export markets for agricultural products in the last half of the twentieth century. However, this strategy did not adequately anticipate the developing world's ability to feed itself. Even China, often viewed as an unlikely candidate for self-sufficiency because of its burgeoning

population of over one billion people, has in recent years become a net exporter of agricultural products.

Recognizing that overproduction threatens the stability of agriculture, the US government instituted a program called the Conservation Reserve Program to deliberately remove marginal lands from production. Producers are allowed to grow grasses or trees on enrolled acreage but cannot harvest this biomass. Almost 34 million acres were enrolled in this program in 2001 compared to about 900 million acres in production. Millions of additional acres are currently devoted to low productivity uses such as pasturage or woodlots that could provide additional land for the production of feedstocks for biobased products. Thus, devoting some land to biorenewable resources poses no immediate threat to food prices in the United States or to feeding the developing countries of the world.

1.4.4 Rural Development

The impact of modern agriculture has not been completely positive. Increases in labor productivity in agriculture have reduced labor costs but contributed to the depopulation of rural communities. Improvements in transportation have expanded opportunities for trade but put US farmers in direct competition with producers in developing nations, where land values are a fraction of what they are in the United States. The highly integrated agricultural processing industry is successful in capturing value from agriculture, of which producers share little. Whereas return in investment in the food processing industry is typically 15%, production agriculture rarely yields returns greater than 1–3%.

As a result, agriculture in developed nations is increasingly dependent on government subsidies to be viable. In the United States, government payments represent in excess of 50% of gross income for typical producers. Farm subsidies in 1997 reached $23 billion. Despite this assistance, producers are increasingly turning to off-farm jobs for supplemental income to support their families. US farming has also consolidated during the twenty-first century, with a larger share of production being attributed to a small number of very large (and often corporate) farmers in an effort to reduce costs via economies of scale.

Both producers and rural communities are looking for new opportunities to boost income and economic development. Development of crops for new markets, especially those that are processed locally into value-added products, would provide significant opportunities for rural development. US biofuels policy has already proven very successful in this regard, with 40% of the US corn crop now being diverted to a high-value fuel ethanol industry that consumed only a small fraction of the amount at the turn of the century. Advanced biorenewable pathways could further increase these opportunities by providing markets for agricultural residues and other waste products, providing a new revenue stream for producers, and by developing higher-value products from existing feedstocks.

1.5 Challenges in Using Biorenewable Resources

Biorenewable resources have a number of disadvantages compared to the fossil resources with which they compete. These include the fact that most biorenewable resources are solid materials of low bulk density, high moisture content, low heating value, and high oxygen content compared to fossil fuels.

The solid nature of biomass is both blessing and curse. Solids are easily collected by hand and can be stored in bins. These advantages were especially important to early human societies, which did not have technology to handle large quantities of liquids and gases. However, solids are notoriously difficult to handle and process in the automated industries of the modern world.

Gases and liquids can be moved hundreds and even thousands of miles through pipelines and stored in tanks with a minimum of human intervention. These fluids do not clog pumps and pipes unless they are carrying solids along with them. The flow of gases and liquids are easily metered with relatively simple instruments and their flow rates can be regulated by the turn of a valve. Gases and liquids can be rapidly and easily dispersed or mixed, which allows them to be readily processed into heat, power, fuels, and chemicals.

Monolithic solids, of course, do not have the property of flow that expedites the handling of gases and solids. However, if solids are broken up into small particles and aerated, they acquire flow properties resembling those of liquids, a fact that has been widely exploited in the twentieth century. Grain is sucked from the holds of ships by giant vacuum cleaner-like devices rather than carried up in 50 kg sacks on the backs of stevedores. Coal is blown as fine powders into giant steam boilers rather than shoveled onto grates by firemen. Even the backbreaking work of shoveling snow from driveways has been replaced by snow blowers that chop up the snow and convey it pneumatically.

Nevertheless, the handling of solids remains a problem. The process of converting solids into granular or powdered materials is an energy intensive process—as little as 10% of the energy consumed by crushing, grinding, or cutting machines actually goes into dividing the materials, the rest dissipated as thermal energy. Particulate materials do not flow as smoothly or predictably as gases and liquids. Particles as coarse as woodchips or as fine as flour can easily clog hoppers and transport lines. Solids metering and control devices are not as reliable or available as for gas and liquid flows. Finely divided solids can present special erosion problems and explosion hazards. Solids handling systems are uniformly acknowledged as high maintenance items in industrial processes.

Typically, the density of biomass is so low that the volume rather than the weight of biomass that can be transported will limit the capacity of the transportation systems. Accordingly, the number of trucks or railcars required to supply a conversion facility will increase as the volumetric density of the fuel decreases. For example, a conventional steam power plant with a relatively modest electric power output of 50 MW would require up to 75 tractor-trailer loads of biomass per day

to stoke the boilers compared to as few as 28 weight-limited loads of coal. Similar arguments apply to the size of the boiler. A boiler designed to burn biomass must be much larger than a coal-fired boiler of comparable thermal output because of the lower energy density of biomass compared to coal. The moisture content of green biomass also detracts from its performance as fuel. Freshly harvested biomass can have moisture content of 50% or more. This additional weight needlessly adds to the cost of transporting the fuel to a conversion facility. In some conversion processes, such as anaerobic digestion, high moisture content may be beneficial to the conversion process. In other cases, such as direct combustion, high moisture exacts a high penalty on the conversion process. Field drying is feasible for many biomass crops but may only reduce moisture content from 20% to 25%. For some processes, additional drying at the conversion plant is required. Freshly mined coal also contains moisture: in some western coals it can be as high as 30%. However, moisture is generally much less of a problem in coal.

Biomass must compete with a variety of fossil resources, including petroleum, natural gas, and coal. Since they are both solid fuels, substituting biomass for coal might seem a more competitive entry into energy markets dominated by fossil fuels. However, on a purely thermodynamic basis, biomass is generally inferior to coal. Coals have heating values typically in the range of 23–28 MJ/kg. On a mass basis, the heating values of biomass are 16–20 MJ/kg, which is 20–30% lower than coal. Exacerbating this situation is the significantly lower densities of biomass compared to coal: mined coal has a bulk density of around 880 kg/m^3 compared to 545 kg/m^3 for hybrid poplar logs and 230 kg/m^3 for baled switchgrass. On a volumetric basis, the heating value of biomass is only 20–50% that of coal. Volumetric heating value is an important consideration both in the transport of biomass to a conversion facility and in the conversion process itself.

Most biorenewable resources contain a significant portion of oxygen, up to 45 wt% for lignocellulosic biomass. In contrast, fossil resources contain substantially less oxygen, which may be as high as 25 wt% in lignite coal and virtually absent in natural gas and petroleum. Although "oxygenated" fuels are touted for their environmental performance as motor fuels, in general, chemically bonded oxygen is responsible for the lower heating values of biobased fuels as well as many of the difficulties of substituting biobased chemicals for petroleum-based chemicals. This difficulty can be resolved by removing oxygen from compounds derived from biorenewable resources to yield hydrocarbons, although this increases the energy consumption for the overall process.

1.6 Foundations for a Bioeconomy

An economy built upon biorenewable resources must be able to supply transportation fuels, commodity chemicals, natural fibers for fabrics and papermaking, and energy for process heat and electric power generation. There is precedence for

producing all of these products from biorenewable resources. However, many of the conversion technologies currently do not yield products that are cost-competitive with the fossil-based products that dominate today's markets. This situation is likely to change as technologies improve for producing biobased products, and environmental and political factors make green products from indigenous resources more attractive. The remaining chapters of this book explore various opportunities for making biobased products.

Further Reading

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CHAPTER

2

Fundamental Concepts in Engineering Thermodynamics

2.1 Introduction

Engineering thermodynamics provides the foundation in mass and energy balances essential to understanding bioenergy and biobased products. Accounting for these balances is more complicated than for energy conversion processes that do not include chemical reaction because chemical constituents change and energy is released from the rearrangement of chemical bonds.

This chapter is designed to introduce or reacquaint readers, as appropriate, to fundamental concepts in engineering thermodynamics. The treatment does not pretend to be exhaustive; readers requiring additional background are directed to the list of reference materials at the end of this chapter.

2.2 General Concepts in Mass and Molar Balances

In the absence of chemical reaction, the change in mass of a particular constituent within a control volume is equal to the difference in net mass flow of the constituent entering and exiting the control volume. Figure 2.1 illustrates mass balance for a system consisting of five inlets and five exits. In general, the mass balance for a given chemical constituent can be written in the form:

$$\frac{\mathrm{d}m_{\mathrm{CV}}}{\mathrm{d}t} = \sum_i \dot{m}_i - \sum_e \dot{m}_e \tag{2.1}$$

where m_{CV} is the amount of mass contained within the control volume; $\dot{m}_i$ and $\dot{m}_e$ are, respectively, the rates at which mass enters at i and exists at e, where we allow for the possibility of several inlets and exits. For steady flow conditions, the net

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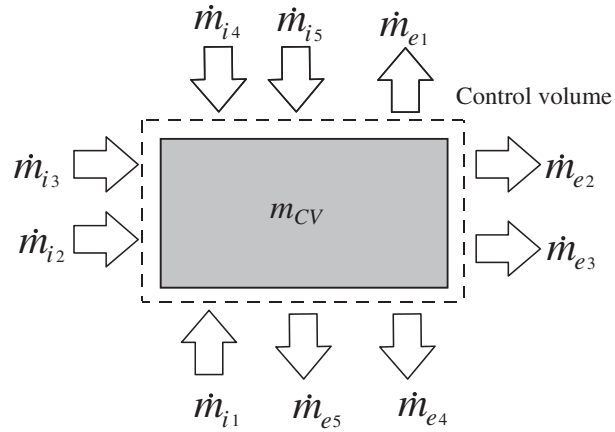

FIG. 2.1 Mass balance on steady-flow control volume with five inlets and five exits.

quantity of mass in the control volume is unchanging with time, and Equation 2.1 can be written as:

$$\sum_i \dot{m}_i = \sum_e \dot{m}_e \tag{2.2}$$

However, when chemical reaction occurs, chemical compounds are not conserved as they flow through the system. For example, methane (CH_4) and oxygen (O_2) entering a combustor are consumed and replaced by carbon dioxide (CO_2) and water (H_2O):

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{2.3}$$

Accordingly, mass balances cannot be written for methane and oxygen using either Equation 2.1 (unsteady flow) or Equation 2.2 (steady flow). Although chemical compounds are not conserved, the chemical elements making up these compounds are conserved; thus, elemental mass balances can be written.

In the case of the reaction of CH_4 with O_2, mass balances can be written for the chemical elements carbon (C), hydrogen (H), and oxygen (O). However, because chemical compounds react in distinct molar proportions, it is usually more convenient to write *molar* balances on the elements.

Recall that a mole of any substance is the amount of mass of that substance that contains as many individual entities (whether atoms, molecules, or other particles), as there are atoms in 12 mass units of carbon-12. For engineering systems, it is usually more convenient to work with kilograms as the unit of mass; thus, for this

measure kilomole (kmol) will be employed instead of the gram-mole (gmol) that often appears in chemistry books. The number of kilomoles of a substance, n, is related to the number of kilograms of a substance, m, by its molecular weight, M (kg/kmol):

$$n = \frac{m}{M} \tag{2.4}$$

On a molar basis, it is straightforward to account for the mass changes that occur during chemical reactions: an overall chemical reaction is written that is supported by molar balances on the elements appearing in the reactant and product chemical compounds.

Example: One kilogram of methane reacts with air. (a) If all of the methane is to be consumed, how many kilograms of air will be required? (b) How many kilograms of carbon dioxide, water, and nitrogen will appear in the products?

One kilogram of methane, with a molecular weight of 16, is calculated to be 1/16 kmol using Equation 2.4. Air is approximated as 79% nitrogen and 21% oxygen on a molar basis. The overall chemical reaction can be written as:

$$\left(\frac{1}{16}\right) CH_4 + a\left(O_2 + \frac{0.79}{0.21}N_2\right) \rightarrow x\,CO_2 + y\,H_2O + z\,N_2$$

where a is the number of kilomoles of oxygen required to consume 1/16 kilomole of CH_4 and x, y, and z are the kilomoles of CO_2, H_2O, and N_2, respectively, in the products. The unknowns in this equation can be found from molar balances on the elements C, H, O, and N:

$$\text{carbon: } \frac{1}{16} = x \text{ (kmol)}$$

$$\therefore m_{CO_2} = n_{CO_2} \times M_{CO_2} = \frac{1}{16} \times 44 = 2.75 \text{ kg}$$

$$\text{hydrogen: } \frac{1}{16} \times 4 = 2y$$

$$y = \frac{1}{8}\text{(kmol)}$$

$$\therefore m_{H_2O} = n_{H_2O} \times M_{H_2O} = \frac{1}{8} \times 18 = 2.25 \text{ kg}$$

$$\text{oxygen: } 2a = 2x + y = 2 \times \frac{1}{16} + \frac{1}{8} = \frac{1}{4}$$

$$a = \frac{1}{8}(\text{kmol})$$

$$\therefore m_{O_2} = n_{O_2} \times M_{O_2} = \frac{1}{8} \times 32 = 4 \text{ kg}$$

$$\text{nitrogen: } \frac{0.79}{0.21}a = \frac{0.79}{0.21} \times \frac{1}{8} = 0.47 = z \text{ (kmol)}$$

$$\therefore m_{N_2} = n_{N_2} \times M_{N_2} = 0.47 \times 28 = 13.2 \text{ kg}$$

A check shows that 18.2 kg of methane and air are converted into 18.2 kg of products in the form of carbon dioxide, water, and nitrogen, as expected from mass conservation.

Mixtures of reactants or products are conveniently described on the basis of either mass fractions or mole fractions. If a mixture consists of N constituents, then the total mass, m, and total number of moles, n, are given by:

$$m = m_1 + m_2 + \cdots + m_N = \sum_{i=1}^{N} m_i \tag{2.5}$$

$$n = n_1 + n_2 + \cdots + n_N = \sum_{i=1}^{N} n_i \tag{2.6}$$

The mass fraction, y_i, of the ith constituent of a mixture is equal to:

$$y_i = \frac{m_i}{m} \tag{2.7}$$

Mass fractions are sometimes presented as percentages by multiplying by 100 and assigning units of weight percent (wt%). The mole fraction, x_i, of the ith constituent of a mixture is equal to:

$$x_i = \frac{n_i}{n} \tag{2.8}$$

Mole fractions are sometimes presented as percentages by multiplying by 100 and assigning units of mole percent (mol%).

Mole fractions are useful in calculating partial pressures, p_i, of the constituents of a gas mixture:

$$p_i = x_i p$$

where p is the total pressure of the mixture:

$$\sum_i^N p_i = \sum_i^N x_i p = p \sum_i^N x_i = p$$

The apparent molecular weight of a mixture, M, can be calculated from the molecular weights of each of the constituents, M_i:

$$M = \frac{m}{n} = \frac{\sum_{i=1}^{N} m_i}{n} = \frac{\sum_{i=1}^{N} n_i M_i}{n} = \sum_{i=1}^{N} \frac{n_i}{n} M_i = \sum_{i=1}^{N} x_i M_i \tag{2.9}$$

It is often useful to convert from mass fractions to mole fractions and vice versa:

$$x_i = \frac{n_i}{n} = \frac{\dfrac{m_i}{M_i}}{\sum_{i=1}^{N} \dfrac{m_i}{M_i}} = \frac{\dfrac{m_i/m}{M_i}}{\sum_{i=1}^{N} \dfrac{m_i/m}{M_i}} = \frac{\dfrac{y_i}{M_i}}{\sum_{i=1}^{N} \dfrac{y_i}{M_i}} \tag{2.10}$$

$$y_i = \frac{m_i}{m} = \frac{n_i M_i}{\sum_{i=1}^{N} n_i M_i} = \frac{(n_i/n) M_i}{\sum_{i=1}^{N} (n_i/n) M_i} = \frac{x_i M_i}{\sum_{i=1}^{N} x_i M_i} \tag{2.11}$$

Example: The combustion of 1 kg of methane requires 17.2 kg of air (4 kg of oxygen and 13.2 kg of nitrogen). As shown in the previous example, the products of combustion are 2.75 kg of carbon dioxide, 2.25 kg of water, and 13.2 kg of nitrogen. Calculate the mass fractions of products. From the mass fractions, calculate the mole fractions. Use the mole fractions to calculate the apparent molecular weight of the product mixture.

Mass of products:

$$m = \sum_{i=1}^{N} m_i = m_{CO_2} + m_{H_2O} + m_{N_2} = 2.75 \text{ kg} + 2.25 \text{ kg} + 13.2 \text{ kg} = 18.2 \text{ kg}$$

Mass fractions of products:

$$y_{CO_2} = \frac{m_{CO_2}}{m} = \frac{2.75}{18.2} = 0.151; y_{H_2O} = \frac{m_{H_2O}}{m} = \frac{2.25}{18.2} = 0.124;$$
$$y_{N_2} = \frac{m_{N_2}}{m} = \frac{13.2}{18.2} = 0.725$$

Mole fractions of products from the mass fractions calculated above:

$$x_{CO_2} = \frac{\frac{y_{CO_2}}{M_{CO_2}}}{\sum_{i=1}^{N} \frac{y_i}{M_i}} = \frac{\frac{0.151}{44}}{\frac{0.151}{44} + \frac{0.124}{18} + \frac{0.725}{28}} = \frac{0.00343}{0.0362} = 0.0947$$

$$x_{H_2O} = \frac{\frac{y_{H_2O}}{M_{H_2O}}}{\sum_{i=1}^{N} \frac{y_i}{M_i}} = \frac{\frac{0.124}{18}}{0.0362} = 0.190; \; x_{N_2} = \frac{\frac{y_{N_2}}{M_{N_2}}}{\sum_{i=1}^{N} \frac{y_i}{M_i}} = \frac{\frac{0.725}{28}}{0.0362} = 0.715$$

Apparent molecular weight from the mole fractions calculated above:

$$M = \sum_{i=1}^{N} x_i M_i = x_{CO_2} M_{CO_2} + x_{H_2O} M_{H_2O} + x_{N_2} M_{N_2} = 0.0947 \times 44$$
$$+ 0.190 \times 18 + 0.715 \times 28 = 27.6 \, \text{kg/kmol}$$

Mass and molar balances are extremely important in evaluating the progress of chemical reactions and in designing chemical reactors. A number of different measures have been devised for evaluating reactant ratios and the extent of chemical reactions.

2.2.1 Mass and Molar Balances Applied to Combustion and Gasification

For combustion and gasification processes, it is useful to compare the actual oxygen provided to the fuel to the amount theoretically required for complete oxidation (the stoichiometric requirement). The fuel–oxygen ratio, F/O, is defined as the mass of fuel per the mass of oxygen consumed (a molar fuel–oxygen ratio is also sometimes defined). Another frequently used ratio is the equivalence ratio, ϕ:

$$\varphi = \frac{(F/O)_{\text{actual}}}{(F/O)_{\text{stoichiometric}}} \tag{2.12}$$

This ratio is less than unity for fuel-lean conditions and greater than unity for fuel-rich conditions. For combustion reactions, two other relationships are also useful, which can be calculated on either mass or molar bases:

$$\text{Theoretical air (\%)} = \left(\frac{\text{actual air}}{\text{stoichiometric air}}\right) \times 100 \tag{2.13}$$

$$\text{Excess air (\%)} = \frac{(\text{actual air} - \text{stoichiometric air}) \times 100}{\text{stoichiometric air}} \tag{2.14}$$

2.2.2 Mass and Molar Balances Applied to Reaction Conversion, Yield, and Selectivity

In evaluating the changes that actually take place during chemical reaction, three quantities are particularly useful: conversion, yield, and selectivity. Conversion is the amount of reactant that is transformed into products during a reaction. The relative conversion, X (not to be confused with mole fractions x_i), is the ratio of the change in the amount of reactant to the initial amount of reactant. It is readily calculated by comparing the initial mass of reactant ($m_{\text{r initial}}$) to the final mass of reactant ($m_{\text{r final}}$):

$$X = \frac{m_{\text{r initial}} - m_{\text{r final}}}{m_{\text{r initial}}} \tag{2.15}$$

Notice that both the numerator and the denominator of Equation 2.15 are based on amounts of reactant, which means it could also be calculated from the initial moles of reactant ($n_{\text{r initial}}$) and the final moles of reactant ($n_{\text{r final}}$):

$$X = \frac{n_{\text{r initial}} - n_{\text{r final}}}{n_{\text{r initial}}} \tag{2.16}$$

Conversion is often presented on a percentage basis by multiplying by 100. Of course, a reaction may involve more than one reactant, in which case the reactant which limits the extent of reaction is considered in calculating conversion.

Yield is the amount of a particular product formed from a reaction. The relative yield Y (not to be confused with mass fractions y_i) can be calculated on either a mass or molar basis, but different operational definitions are required in these two cases, because they involve both reactants and products in their calculation. Relative *mass* yield is calculated as the ratio of the mass of product, m_{p}, to the mass of reactant, m_{r}:

$$Y(\text{mass basis}) = \frac{m_{\text{p}}}{m_{\text{r}}} \tag{2.17}$$

This ratio is often presented as a percentage by multiplying by 100 and assigning dimensions of wt% to make clear that it is on a mass basis. Mass yields are straightforward to calculate from gravimetric yield data. They are also frequently preferred when calculating processing costs.

The relative *molar* yield is also written as a ratio of the amount of product to the amount of reactant, but since moles are not conserved in a reaction, the expression must be adjusted to account for the stoichiometric requirement of reactant to produce a mole of product:

$$Y(\text{molar basis}) = \left(\frac{n_\text{p}}{n_\text{r}}\right)\phi \tag{2.18}$$

where ϕ, the stoichiometric factor, is the moles of reactant required stoichiometrically to produce the observed moles of product:

$$\phi = \frac{n_{\text{r stoich}}}{n_\text{p}} \tag{2.19}$$

Substituting Equation 2.19 into Equation 2.18 reveals that relative molar yield can be equivalently stated as the moles of reactant required stoichiometrically to produce the observed products divided by the actual moles of reactant:

$$Y(\text{molar basis}) = \left(\frac{n_\text{p}}{n_\text{r}}\right)\phi = \left(\frac{n_\text{p}}{n_\text{r}}\right) \times \left(\frac{n_{\text{r stoich}}}{n_\text{p}}\right) = \frac{n_{\text{r stoich}}}{n_\text{r}} \tag{2.20}$$

The relative molar yield is also commonly presented as a percentage by multiplying by 100 and assigning a unit of mol% to make clear that it is on a molar basis. Molar yields are frequently preferred to mass yields when evaluating chemical pathways for reactions.

Often the relative molar yield is defined in terms of the actual moles of product formed compared to the theoretically expected moles of product as determined from the stoichiometric formula for the reaction:

$$Y(\text{molar basis}) = \frac{n_\text{p}}{n_{\text{p stoic}}} \tag{2.21}$$

Equations 2.20 and 2.21 are functionally equivalent.

Example: One kilomole of glucose ($C_6H_{12}O_6$) is fermented to produce 1.75 kmol of ethanol (C_2H_5OH). Calculate both mass and molar relative yields of ethanol. Show that Equations 2.18 and 2.19 give the same relative molar yield.

Relative mass yield:

$$m_{\text{glucose}} = 1 \text{ kmol} \times (180 \text{ kg/kmol}) = 180 \text{ kg};$$

$$m_{\text{ethanol}} = 1.75 \text{ kmol} \times (46 \text{ kg/kmol}) = 80.5 \text{ kg}$$

$$Y_{\text{ethanol}}(\text{mass basis}) = \frac{m_{\text{p}}}{m_{\text{r}}} = \frac{m_{\text{ethanol}}}{m_{\text{glucose}}} = \frac{80.5 \text{ kg}}{180 \text{ kg}} \times 100 = 44.7\text{wt\%}$$

From stoichiometrically balanced reaction for ethanol fermentation, we can see that as much as 2 kmol of ethanol could have been produced:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

Complete conversion to ethanol would have given a mass yield of 51.1%, the remaining mass having been converted to CO_2.

Relative molar yield:
One kilomole of glucose is required to produce 2 kmol of ethanol; thus, the stoichiometric factor is:

$$\phi = \frac{\text{stoichiometric requirement for moles of reactant}}{\text{moles of product}} = \frac{1}{2}$$

Substituting into Equation 2.20 yields:

$$Y(\text{molar basis}) = \left(\frac{n_{\text{p}}}{n_{\text{r}}}\right)\phi = \left(\frac{1.75}{1}\right) \times \frac{1}{2} \times 100 = 87.5\%$$

The relative molar yield given by Equation 2.21 gives the same result as above:

$$Y(\text{molar basis}) = \frac{n_{\text{p}}}{n_{\text{p stoic}}} = \left(\frac{1.75}{2}\right) \times 100 = 87.5\%$$

In contrast to mass yield, notice that molar relative yield would have reached 100% if the glucose had been completely converted to ethanol. The fact that this was not achieved indicates that other metabolic reactions produced additional products, such as acetic acid.

Selectivity, *S*, can be defined two different ways. Sometimes it is useful to define selectivity as the ratio of moles of desired product to moles of undesired products. Alternatively, selectivity can be written as the ratio of moles of desired product to

the moles of the reactant converted. For mass selectivities, this is simply the ratio of the mass of specific product to the mass of the reactant converted:

$$S_{\mathrm{p}_i}(\text{mass basis}) = \left(\frac{m_{\mathrm{p}_i}}{m_{\mathrm{r\,converted}}}\right) \tag{2.22}$$

where $m_{\mathrm{p}i}$ is the mass of the ith product and $m_{\mathrm{r\,converted}}$ is the mass of the reactant converted. For molar selectivities, because both reactants and products are involved in the calculation, the definition must be adjusted to account for the stoichiometric amount of the reactant required to produce a mole of product:

$$S_{\mathrm{p}_i}(\text{molar basis}) = \left(\frac{n_{\mathrm{p}_i}}{n_{\mathrm{r\,converted}}}\right)\phi_{\mathrm{p}_i} \tag{2.23}$$

where $n_{\mathrm{p}i}$ is the moles of the ith product and $\phi_{\mathrm{p}i}$ is the stoichiometric amount of the reactant required to produce $n_{\mathrm{p}i}$:

$$\phi_{\mathrm{p}_i} = \frac{n_{\mathrm{r\,stoich}}}{n_{\mathrm{p}i}} \tag{2.24}$$

This ratio is often presented as a percentage by multiplying by 100 and assigning a unit of mol% to make clear that it is on a molar basis. Occasionally, selectivity is defined in terms of a certain class of products, in which case the denominator of Equation 2.23 refers to only that amount of the reactant that is converted to the specified class of products.

Given the conversion of a reactant and the selectivity of the products, the yields of specific products can be calculated by combining Equation 2.16 with Equation 2.23:

$$\begin{aligned} Y_{\mathrm{p}_i}(\text{molar basis}) = X \cdot S_{\mathrm{p}_i} &= \left(\frac{n_{\mathrm{r\,initial}} - n_{\mathrm{r\,final}}}{n_{\mathrm{r\,initial}}}\right)\left(\frac{n_{\mathrm{p}_i}}{n_{\mathrm{r\,initial}} - n_{\mathrm{r\,final}}}\right)\phi_{\mathrm{p}_i} \\ &= \frac{n_{\mathrm{p}_i}}{n_{\mathrm{r\,initial}}}\phi_{\mathrm{p}_i} \end{aligned} \tag{2.25}$$

Example: One hundred kilograms of cellulose are mixed with water and a catalyst and heated to a high temperature and pressure in a closed vessel (a process called hydrothermal processing) and undergoes a combination of hydrolysis (water adding) and dehydrating (water removing) reactions. At the end of the experiment, 10 kg of unreacted cellulose ($C_6H_{10}O_5$) and 8.9 kg of char (solid carbon) are filtered from the aqueous solution, which is found to contain 44.4 kg of glucose ($C_6H_{12}O_6$), 23.3 kg of hydroxymethyl furfural (HMF) ($C_6H_6O_3$), and 13.3 kg of

water. Calculate the conversion of cellulose, the selectivity of glucose, HMF, and char products, and the yield of glucose for this process.

Cellulose conversion:

$$X = \frac{m_{\text{r initial}} - m_{\text{r final}}}{m_{\text{r initial}}} = \frac{100\text{ kg} - 10\text{ kg}}{100\text{ kg}} x100 = 90\%$$

To calculate selectivities on a molar basis, products must first be converted from mass to moles:

Glucose ($C_6H_{12}O_6$): $M_{\text{glucose}} = 6 \times 12 + 12 \times 1 + 6 \times 16 = 180\text{ kg/kmol}$

$$n_{\text{glucose}} = \frac{44.4\text{ kg}}{180\,\text{kg/kmol}} = 0.247\text{ kmol}$$

HMF ($C_6H_6O_3$): $M_{\text{HMF}} = 6 \times 12 + 6 \times 1 + 3 \times 16 = 126\,\text{kg/kmol}$

$$n_{\text{HMF}} = \frac{23.3\text{ kg}}{126\,\text{kg/kmol}} = 0.185\text{ kmol}$$

Char (carbon): $M_{\text{char}} = 12\,\text{kg/kmol}$

$$n_{\text{char}} = \frac{8.9\text{ kg}}{12\,\text{kg/kmol}} = 0.742\text{ kmol}$$

Also, the initial and final moles of cellulose must be determined:

Initial cellulose ($C_6H_{10}O_5$): $M_{\text{cellulose}} = 6 \times 12 + 10 \times 1 + 5 \times 16 = 162\,\text{kg/kmol}$

$$n_{\text{cellulose initial}} = \frac{100\text{ kg}}{162\,\text{kg/kmol}} = 0.617\text{ kmol}$$

Final cellulose ($C_6H_{10}O_5$): $n_{\text{cellulose final}} = \frac{10\text{ kg}}{162\,\text{kg/kmol}} = 0.0617\text{ kmol}$

Next, the stoichiometric factors for each of the products must be calculated, which requires identification of the reactions of cellulose that produce each of the products:

Hydrolysis of cellulose to glucose: $C_6H_{10}O_5 + H_2O \rightarrow C_6H_{12}O_6$

Dehydration of cellulose to HMF: $C_6H_{10}O_5 \rightarrow C_6H_6O_3 + 3H_2O$

Dehydration of cellulose to char: $C_6H_{10}O_5 \rightarrow 6C + 5H_2O$

From these, the stoichiometric factors can be calculated:

$$\phi_{\text{glucose}} = \frac{n_{\text{cellulose stoich}}}{n_{\text{glucose}}} = \frac{1}{1} = 1$$

$$\phi_{\text{HMF}} = \frac{n_{\text{cellulose stoich}}}{n_{\text{HMF}}} = \frac{1}{1} = 1$$

$$\phi_{\text{char}} = \frac{n_{\text{cellulose stoich}}}{n_{\text{char}}} = \frac{1}{6} = 0.167$$

Selectivities for products on a molar basis can then be calculated:

$$S_{\text{glucose}} = \left(\frac{n_{\text{glucose}}}{n_{\text{cellulose initial}} - n_{\text{cellulose final}}}\right)\phi_{\text{glucose}} = \frac{0.247 \text{ kmol}}{0.617 \text{ kmol} - 0.0617 \text{ kmol}} \times 1 \times 100 = 44.5\%$$

$$S_{\text{HMF}} = \left(\frac{n_{\text{HMF}}}{n_{\text{cellulose initial}} - n_{\text{cellulose final}}}\right)\phi_{\text{HMF}} = \left(\frac{0.185 \text{ kmol}}{0.617 \text{ kmol} - 0.0617 \text{ kmol}}\right) \times 1 \times 100 = 33.3\%$$

$$S_{\text{char}} = \left(\frac{n_{\text{char}}}{n_{\text{cellulose initial}} - n_{\text{cellulose final}}}\right)\phi_{\text{char}} = \left(\frac{0.742 \text{ kmol}}{0.617 \text{ kmol} - 0.0617 \text{ kmol}}\right) \times 0.167 \times 100 = 22.3\%$$

Notice that the selectivities on a molar basis sum to 100%, which should be the case if all products are accounted for. The yield of glucose is calculated from the relative conversion of cellulose, X, and the selectivity for glucose, S_{glucose}:

$$Y_{\text{glucose}}(\text{molar basis}) = X \cdot S_{\text{glucose}} = 0.90 \times 0.445 \times 100 = 40.05 \text{ mole\%}$$

In reactions of organic compounds, it is often desirable to determine how much carbon in the reactants is converted to particular products. Thus, carbon yield, Y_C, is defined as the amount of carbon in a specific product to the carbon in the reactant. Since moles of elements are conserved during a reaction, this quantity can be calculated using either mass or molar quantities:

$$Y_{C,pi} = \frac{n_{C,p_i}}{n_{C,r}} = \frac{n_{C,p_i} M_C}{n_{C,r} M_C} = \frac{m_{C,p_i}}{m_{C,r}} \tag{2.26}$$

where the subscript C on the molar and mass terms refers to carbon. Furthermore, the carbon yield can be related to the relative mass yield Y_i:

$$Y_{C,p_i} = \frac{m_{C,p_i}}{m_{C,r}} = \left(\frac{m_{C,p_i}/m_{p_i}}{m_{C,r}/m_r}\right)\left(\frac{m_{p_i}}{m_r}\right) = \left(\frac{f_{C,p_i}}{f_{C,r}}\right) Y_i (\text{mass basis}) \tag{2.27}$$

where $f_{C,pi}$ is the mass fraction of the carbon in the ith product and $f_{C,r}$ is the mass fraction of the carbon in the reactant.

A similar relationship exists between the carbon selectivity and the mass selectivity:

$$\begin{aligned} S_{C,p_i} &= \frac{n_{C,p_i}}{n_{C,r\,converted}} = \frac{m_{C,p_i}/M_C}{m_{C,r\,converted}/M_C} = \frac{m_{C,p_i}}{m_{C,r\,converted}} \\ &= \left(\frac{m_{C,p_i}/m_{p_i}}{m_{C,r\,converted}/m_{r\,converted}}\right)\left(\frac{m_{p_i}}{m_{r\,converted}}\right) \\ &= \left(\frac{f_{C,p_i}}{f_{C,r}}\right) S_{p_i} (\text{mass basis}) \end{aligned} \tag{2.28}$$

where $m_{C,r\ converted}$ is the mass of the carbon converted in the reactant.

Carbon yield can be calculated from the reactant conversion and the carbon selectivity:

$$Y_{C,p_i} = X \cdot S_{C,p_i} = \left(\frac{n_{C,r\,converted}}{n_{C,r}}\right)\left(\frac{n_{C,p_i}}{n_{C,r\,converted}}\right) = \frac{n_{C,p_i}}{n_{C,r}} \tag{2.29}$$

Example: Calculate the carbon selectivity and the carbon yield for each of the products (glucose, HMF, and char) for the previous example of hydrothermally processing of cellulose.

The relative conversion of cellulose was stated in the previous problem to be 90%. Mass selectivities are first calculated using Equation 2.22, which recognizes that only 90% of the 100 kg of cellulose is converted to products:

$$S_{\text{glucose}}(\text{mass basis}) = \left(\frac{m_{\text{glucose}}}{m_{\text{cellulose converted}}}\right) = \left(\frac{44.4\text{ kg}}{90\text{ kg}}\right) \times 100 = 49.3\%$$

$$S_{\text{HMF}}(\text{mass basis}) = \left(\frac{m_{\text{HMF}}}{m_{\text{cellulose converted}}}\right) = \left(\frac{23.3\text{ kg}}{90\text{ kg}}\right) \times 100 = 25.9\%$$

$$S_{\text{carbon}}(\text{mass basis}) = \left(\frac{m_{\text{carbon}}}{m_{\text{cellulose converted}}}\right) = \left(\frac{8.9\text{ kg}}{90\text{ kg}}\right) \times 100 = 9.9\%$$

Notice that selectivities based on mass do not sum to 100%, because product water is not included in the calculation.

To calculate selectivities on a molar basis, the mass fractions of the carbon in the reactant and the products must first be determined:

Cellulose ($C_6H_{10}O_5$): $$f_{\text{C,cellulose}} = \frac{6 \times 12}{(6 \times 12 + 10 \times 1 + 5 \times 16)} = 0.44$$

Glucose ($C_6H_{12}O_6$): $$f_{\text{C,glucose}} = \frac{6 \times 12}{(6 \times 12 + 12 \times 1 + 6 \times 16)} = 0.40$$

HMF ($C_6H_6O_3$): $$f_{\text{C,HMF}} = \frac{6 \times 12}{(6 \times 12 + 6 \times 1 + 3 \times 16)} = 0.57$$

Char (C): $$f_{\text{C,Char}} = \frac{1 \times 12}{1 \times 12} = 1.00$$

These carbon mass fractions can be combined with the previously determined mass selectivities of the products using Equation 2.28:

$$S_{\text{C,glucose}} = \left(\frac{f_{\text{C, glucose}}}{f_{\text{C, cellulose}}}\right) S_{\text{glucose}}(\text{mass basis}) = \left(\frac{0.40}{0.44}\right) \times 49.3 \times 100 = 44.8\%$$

$$S_{\text{C,HMF}} = \left(\frac{f_{\text{C, HMF}}}{f_{\text{C, cellulose}}}\right) S_{\text{HMF}}(\text{mass basis}) = \left(\frac{0.57}{0.44}\right) \times 25.9\% = 33.5\%$$

$$S_{\text{C,Char}} = \left(\frac{f_{\text{C, Char}}}{f_{\text{C, cellulose}}}\right) S_{\text{Char}}(\text{mass basis}) = \left(\frac{1.00}{0.44}\right) \times 9.9\% = 22.5\%$$

Molar carbon yields are then calculated from Equation 2.29:

$$Y_{\mathrm{C,glucose}} = X \cdot S_{\mathrm{C,glucose}} = 0.9 \times 44.8 = 40.3\%$$

$$Y_{\mathrm{C,HMF}} = X \cdot S_{\mathrm{C,HMF}} = 0.9 \times 33.5 = 30.2\%$$

$$Y_{\mathrm{C,Char}} = X \cdot S_{\mathrm{C,Char}} = 0.9 \times 22.5 = 20.3\%$$

These do not sum to 100% because only 90% of the cellulose is converted into products.

2.3 General Concepts in Energy Balances

In the absence of chemical reaction, the net change in the stored energy within a control volume is given by the net flow of the energy into the control volume in the form of heat and work as well as kinetic energy, potential energy, and enthalpy associated with mass flowing into and out of the control volume. Figure 2.2 illustrates the energy balance for a control volume with two inlets and one outlet and with work transferred in and heat transferred out. More generally, a system undergoing steady flow processes can be described by an energy balance of the form:

$$\frac{\mathrm{d}E_{\mathrm{CV}}}{\mathrm{d}t} = \dot{Q}_{\mathrm{CV}} - \dot{W}_{\mathrm{CV}} + \sum_i \dot{m}_{\mathrm{i}} \left(h_{\mathrm{i}} + \tfrac{1}{2} V_{\mathrm{i}}^2 + g z_{\mathrm{i}}\right) - \sum_e \dot{m}_{\mathrm{e}} \left(h_{\mathrm{e}} + \tfrac{1}{2} V_{\mathrm{e}}^2 + g z_{\mathrm{e}}\right) \tag{2.30}$$

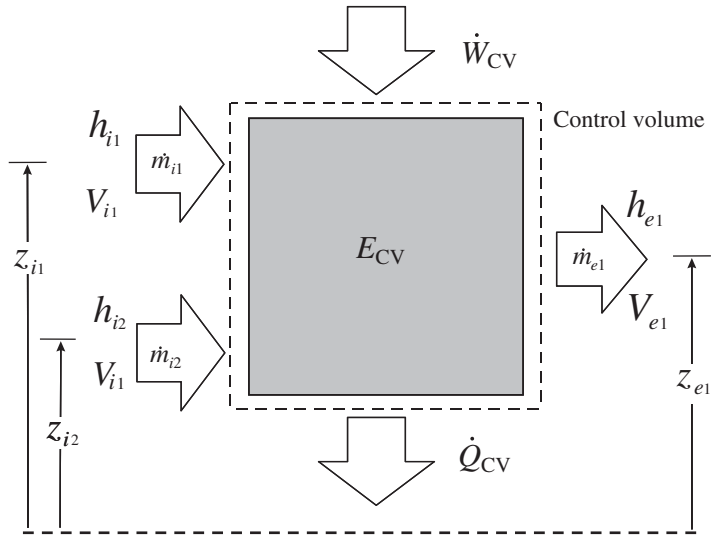

FIG. 2.2 Energy balance on steady-flow control volume with two inlets and one exit.

where E_{CV} is the stored energy in the control volume, $\dot{Q}_{CV}$ and $\dot{W}_{CV}$ are the rates at which heat and work cross the control volume boundary, h is enthalpy, V is velocity, and z is elevation with respect to an arbitrary datum for the mass flows at the inlet, i, and outlet, e. In steady flow, with a single inlet and single outlet and no velocity or elevation changes in the system, Equation 2.30 simplifies to:

$$\dot{Q}_{CV} - \dot{W}_{CV} = \dot{m}\,(h_e - h_i) \tag{2.31}$$

However, for a chemically reacting system, this formulation of an energy balance does not take into account changes in the chemical composition of the system nor the chemical energy absorbed or released during these reactions. Like mass conservation, it is more convenient to present energy conservation in a molar formulation rather than a mass formulation when chemical reaction occurs. The intensive property enthalpy, h, with units of kJ/kg, is replaced by the intensive property molar enthalpy, $\bar{h}$, with units of kJ/kmol. Enthalpy, like other properties, can be evaluated as a function of two other independent properties, usually taken to be temperature and pressure. In the case of ideal gases, enthalpy is independent of pressure and can be expressed solely as a function of temperature. Table 2.1 includes an abbreviated collection of molar enthalpies of selected ideal gases as a function of temperature. More extensive collections are available in thermodynamics textbooks.

Energy conservation on a molar basis for a steady flow system consisting of one inlet for reactants r and one outlet for products p (and neglecting velocity or elevation changes) is of the form:

$$\dot{Q}_{CV} - \dot{W}_{CV} = \sum_{p} \dot{n}_p \bar{h}_p - \sum_{r} \dot{n}_r \bar{h}_r \tag{2.32}$$

where $\dot{n}$ specifies the molar flow rate of a chemical constituent and the summation is over all the products p at the exit or all the reactants r at the inlet. Integrated over a finite time interval, this equation takes the form:

$$Q_{CV} - W_{CV} = \sum_{p} n_p \bar{h}_p - \sum_{r} n_r \bar{h}_r \tag{2.33}$$

where Q_{CV} and W_{CV} are the amounts of heat and work done over a designated time interval and n_r and n_p are the moles of the reactants and the products, respectively, crossing the control surface in the time interval. A convenient shorthand is to designate H_p and H_r as the mixture enthalpies (kJ) of the products and the reactants, respectively, and ΔH as the change in enthalpy between the products and the reactants:

$$\Delta H = H_p - H_r = \sum_{p} n_p \bar{h}_p - \sum_{r} n_r \bar{h}_r \tag{2.34}$$

Table 2.1 Thermodynamic properties for selected gases

T (K), $\bar{h}$ (kJ/kmol), $\bar{S}_0$ (kJ/kmol-K)

	N_2		O_2		H_2O (g)		CO		CO_2		H_2	
T	$\bar{h}$	$\bar{S}_0$	$\bar{h}$	$\bar{S}_0$	$\bar{h}$	$\bar{S}_0$	$\bar{h}$	$\bar{S}_0$	$\bar{h}$	$\bar{S}_0$	$\bar{h}$	$\bar{S}_0$
0	0	0	0	0	0	0	0	0	0	0	0	0
298	8 669	191.50	8 682	205.03	9 904	188.72	8 669	197.54	9 364	213.69	8 468	130.57
500	14 581	206.63	14 770	220.59	16 828	206.41	14 600	212.72	17 678	234.81	14 350	145.63
1000	30 129	228.06	31 389	243.47	35 882	232.60	30 355	234.42	42 769	269.22	29 154	166.11
1500	47 073	241.77	49 292	257.97	57 999	250.45	47 517	248.31	71 078	292.11	44 738	178.72
2000	64 810	251.97	67 881	268.66	82 593	264.57	65 408	258.60	100 804	309.21	61 400	188.30
2500	82 981	260.07	87 057	277.21	108 868	276.29	83 692	266.76	131 290	322.81	78 960	196.13
3000	101 407	266.79	106 780	284.40	136 264	286.27	102 210	273.51	162 226	334.08	97 211	202.78
3250	110 690	269.76	116 827	287.61	150 272	290.76	111 534	276.49	177 822	339.07	106 545	205.77

Substance	Formula	h_f^0 (kJ/kmol)
Carbon	C(s)	0
Hydrogen	H_2	0
Nitrogen	N_2	0
Oxygen	O_2	0
Carbon monoxide	CO	–110 530
Carbon dioxide	CO_2	−393 520
Water (liquid)	H_2O (l)	−285 830
Water (vapor)	H_2O (g)	−241 820
Methane	CH_4	−74 850
Methanol (liquid)	CH_3OH (l)	−238,810
Methanol (vapor)	CH_3OH (g)	−200 890
Ethanol (liquid)	C_2H_5OH (l)	−277 690
Ethanol (vapor)	C_2H_5OH (g)	−235 310

Source: Excerpted from Cengel, Y. and Boles, M. (2010) *Thermodynamics: An Engineering Approach*, 7th edn. McGraw-Hill.

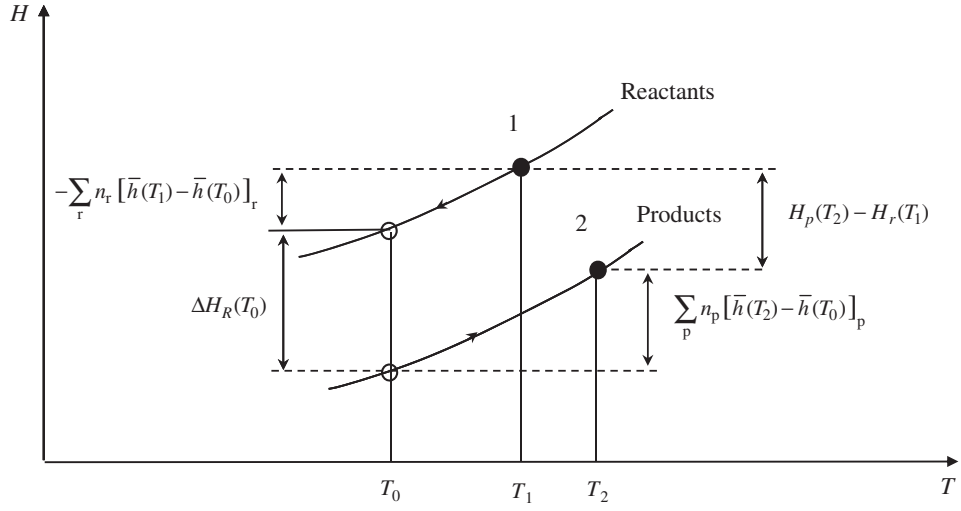

FIG. 2.3 Relationship between mixture enthalpy and temperature for a chemically reacting system.

An enthalpy–temperature diagram, shown in Figure 2.3, is useful in understanding the change in enthalpy that occurs in the presence of a chemical reaction. For a given mixture of reactants, say methane and oxygen, there is a unique enthalpy–temperature relationship. Similarly, a unique enthalpy relationship exists for the products of methane oxidation (carbon dioxide and water). It is also easy to understand the enthalpy change that occurs for a constant temperature chemical reaction: reactants at T_o are converted to products at T_o with a release or absorption of energy known as the enthalpy of reaction $\Delta H_R(T_o)$ at temperature T_o. Reactions that release energy (exothermic reactions) have negative enthalpies of reaction, whereas reactions that absorb energy (endothermic reactions) have positive enthalpies of reaction. This situation becomes obvious by inspecting Equation 2.33 and recalling the convention that Q_{cv} is negative for heat flow out of a system.

However, the typical chemical reaction is not isothermal; indeed, many combustion reactions are accompanied by temperature increases of over 1000 K. Thus, enthalpy changes must account for sensible enthalpy changes of the reactants, sensible enthalpy changes for the products, and the release or absorption of heat as a result of the chemical reaction. One way to handle this potentially complicated situation is to visualize the reaction as following the reaction pathway illustrated in Figure 2.3: reactants initially at temperature T_1 are cooled to temperature T_o at which point the reactants undergo isothermal chemical reaction to form the products that are then heated to the final temperature T_2. Thus, the

enthalpy change for non-isothermal chemical reactions can be calculated from the relationship:

$$H_p(T_2) - H_r(T_1) = \sum_p n_p \left[\bar{h}(T_2) - \bar{h}(T_o)\right]_p + \Delta H_R(T_o) - \sum_r n_r \left[\bar{h}(T_1) - \bar{h}(T_o)\right]_r \tag{2.35}$$

where sensible enthalpies, $\bar{h}(T)$, for a variety of chemical substances are available as tabulations of thermodynamic properties of substances. Likewise, enthalpies of reaction at a specified reference temperature, T_o, have been compiled for a number of chemical reactions. In the SI system, T_o is chosen as 298 K for the purpose of tabulating data. Using Equation 2.35, tabulations of sensible enthalpies and enthalpies of reaction can be used to calculate enthalpy changes for reactions under a wide variety of conditions.

Example: One kilomole of biogas produced by anaerobic digestion of animal waste consists of 60% methane and 40% carbon dioxide by volume (i.e., molar basis). The biogas reacts with 1.2 kilomoles of oxygen to form carbon dioxide and water. The enthalpy of reaction for methane is –890 330 kJ/kmol at 298 K. Calculate the enthalpy change if the reactants are at 298 K and the products are at 1500 K.

The complete reaction is:

$$(0.6CH_4 + 0.4CO_2) + 1.2O_2 \rightarrow CO_2 + 1.2H_2O$$

From Table 2.1 the following sensible enthalpies are found:

Temperature (K)	$h_{CH4}(T)$ (kJ/kmol)	$h_{O2}(T)$ (kJ/kmol)	$h_{CO2}(T)$ (kJ/kmol)	$h_{H2O}(T)$ (kJ/kmol)
298	–	8 682	9 364	9 904
1500	–	–	71 078	57 999

Substituting values into Equation 2.35:

$$[1(71\,078 - 9364) + 1.2(57\,999 - 9904)] + 0.6(-890\,330) - [0.6(0) + 0.4(0) + 1.2(0)]$$
$$= -414\,770$$

Thus, 414 770 kJ is released by the combustion of 1 kilomole of biogas under these conditions.

For some well-characterized fuels, such as hydrogen, methane, and ethanol, enthalpies of reaction can be calculated from tabulations of specific enthalpies of formation, $\bar{h}_f^o$, of chemical compounds from their elements at a standard state:

$$\Delta H_R^o = \sum_p n_p \bar{h}_f^o)_p - \sum_r n_r \bar{h}_f^o)_r \tag{2.36}$$

where n_r and n_p are the number of moles of reactants and products for the chemical reaction. Selected values of enthalpies of formation are found in Table 2.1.

Example: Use standard enthalpies of formation to calculate the enthalpy of reaction of liquid ethanol (C_2H_5OH) with oxygen to form carbon dioxide and water vapor.

The stoichiometric reaction is expressed by:

$$C_2H_5OH\,(l) + 3O_2 \rightarrow 2CO_2 + 3H_2O\,(g)$$

From Table 2.1:

Compound	C_2H_5OH (l)	O_2	CO_2	H_2O (g)
$\bar{h}_f^o$ (kJ/kmol)	–277 690	0	–393 520	–241 820
Kilomoles	1	3	2	3

Substituting into Equation 2.36 yields:

$$\Delta H_R^o = 2(-393\,520) + 3(-241\,820) - (-277\,690) - 3(0) = -1\,234\,800\,\text{kJ}$$

Enthalpies of formation are very useful in thermodynamic calculations, but this data is rarely tabulated for biomass because of the wide variability in its composition. However, if higher heating value for a biomass fuel has been determined in a bomb calorimeter, its enthalpy of formation can be determined by summing the enthalpies of formation for the products of combustion and subtracting from this sum the higher heating value.

Example: A sample of switchgrass has an elemental analysis that gives a generic molecular formula of $CH_{1.4}O_{0.8}$ (apparent molecular weight of 26.2 kg/kmol) and its higher heating value is measured to be 18.1 MJ/kg. The combustion of 1 kmol of switchgrass can be represented by:

$$CH_{1.4}O_{0.8} + 0.95O_2 \rightarrow CO_2 + 0.7H_2O\,(\text{liq})$$

The enthalpy of reaction is calculated from the various enthalpies of formation using Equation 2.36:

$$\Delta H_R = h^o_{f\,CO_2} + 0.7h^o_{f\,H_2O(\text{liq})} - \left(h^o_{f\,CH_{1.4}O_{0.8}} + 0.95h^o_{fO_2}\right)$$

$$-18.1\frac{\text{MJ}}{\text{kg}}\left(26.2\,\frac{\text{kg}}{\text{kmol}}\right) = -393.5\frac{\text{MJ}}{\text{kmol}} + 0.7\left(-285.8\frac{\text{MJ}}{\text{kmol}}\right)$$

$$-\left(\Delta h^o_{fCH_{1.4}O_{0.8}} + 0\right)$$

Solving for the enthalpy of formation for $CH_{1.4}O_{0.8}$ yields:

$$h^{\circ}_{fCH_{1.4}O_{0.8}} = -119.3 \frac{MJ}{kmol}$$

This value can be used in various thermodynamic calculations for this switchgrass sample, whether gasification to hydrogen or combustion to flue gas.

Commonly Equations 2.35 and 2.36 are combined to allow calculation of enthalpy changes purely in terms of tabulated sensible enthalpies and enthalpies of formation:

$$\begin{aligned} H_p(T_2) - H_r(T_1) &= \sum_p n_p \left[\bar{h}(T_2) - \bar{h}(T_o)\right]_p + \sum_p n_p \bar{h}^{\circ}_{f})_p - \sum_r n_r \bar{h}^{\circ}_{f})_r \\ &- \sum_r n_r \left[\bar{h}(T_1) - \bar{h}(T_o)\right]_r = \sum_p n_p \left\{\bar{h}^{\circ}_f + \left[\bar{h}(T_2) - \bar{h}(T_o)\right]\right\}_p \\ &- \sum_r n_r \left\{\bar{h}^{\circ}_f + \left[\bar{h}(T_1) - \bar{h}(T_o)\right]\right\}_r \end{aligned} \tag{2.37}$$

Thus, the molar enthalpy for a chemical compound participating in a chemical reaction must include both the enthalpy of formation and the sensible enthalpy change with respect to the reference temperature T_o. Sometimes it is convenient to express changes in enthalpy with Equation 2.34 as long as it is recognized that the molar enthalpies $\bar{h}_p$ and $\bar{h}_r$ in this expression include both the enthalpy of formation and the sensible enthalpy change:

$$\bar{h}_i = \left\{\bar{h}^{\circ}_f + \left[\bar{h}(T) - \bar{h}(T_o)\right]\right\}_i \tag{2.38}$$

Example: One kilomole of hydrogen reacts with one-half kilomole of oxygen at 298 K to form 1 kilomole of water vapor at 1500 K. What is the change in enthalpy for the reaction?

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$$

Compound	H_2	O_2	H_2O (g)
$\bar{h}^{\circ}_f$ (kJ/kmol)	0	0	–241 820
$\bar{h}$(298 K)	8468	8682	9904
$\bar{h}$(1500 K)	–	–	57 999
Kilomoles	1	1/2	1

$$H_{\mathrm{p}}(T_2) - H_{\mathrm{r}}(T_1) = \sum_{\mathrm{p}} n_{\mathrm{p}} \bar{h}_{\mathrm{p}} - \sum_{\mathrm{r}} n_{\mathrm{r}} \bar{h}_{\mathrm{r}} = \sum_{\mathrm{p}} n_{\mathrm{p}} \left\{ \bar{h}_{\mathrm{f}}^{\mathrm{o}} + \left[\bar{h}(T_2) - \bar{h}(T_{\mathrm{o}}) \right] \right\}_{\mathrm{p}}$$
$$- \sum_{\mathrm{r}} n_{\mathrm{r}} \left\{ \bar{h}_{\mathrm{f}}^{\mathrm{o}} + \left[\bar{h}(T_1) - \bar{h}(T_{\mathrm{o}}) \right] \right\}_{\mathrm{r}}$$
$$= 1 \times \{-241\,820 + [57\,999 - 9904]\} - 1$$
$$\times \{0 + [8468 - 8468]\} - \tfrac{1}{2}\{0 + [8682 - 8682]\}$$
$$= -193\,730\ \mathrm{kJ}$$

2.3.1 Thermodynamic Efficiency

The conversion of the chemical energy stored in biomass into more useful forms, such as gaseous and liquid fuels or electrical power, is accompanied by loss of energy to forms that are not easily recovered or utilized. There are many reasons for such losses. Separation processes can inadvertently reject valuable fractions of a feedstock to waste streams. Heat losses can reduce the amount of energy available to energy conversion processes. Entropy production inherent in even ideal processes limits the amount of energy that can be converted into useful forms. Every energy conversion process can be characterized by thermodynamic (or energy) efficiency defined as:

$$\eta = \frac{E_{\mathrm{useful}}}{E_{\mathrm{in}}} \tag{2.39}$$

where E_{in} = all forms of energy entering the conversion process; E_{useful} = useful energy leaving the conversion process.

Energy entering the process includes the chemical enthalpy of the feedstock (E_{feed}) and the heat and power required to process the feedstock (E_{process}). The useful energy leaving the process includes chemical energy of gaseous and liquid fuels, electric power, and heat that can be used external to the process, such as district heating of buildings. If all the input energy was converted into useful energy, energy efficiency would be 1. However, most energy conversion processes have efficiencies substantially less than unity indicating that some energy leaves the process as waste energy (i.e., incompletely converted feedstock or waste heat).

When applied to the thermodynamic performance of heat engines, E_{in} is the heat energy entering the engine, Q_{in}, and E_{useful} is the net mechanical work generated by the engine, W_{net}:

$$\eta = \frac{W_{\mathrm{net}}}{Q_{\mathrm{in}}} \tag{2.40}$$

In the case of electrical power plants, Q_{in} is calculated as the enthalpy of reaction (MJ/kg) multiplied by the mass flow rate of fuel (kg/s), while W_{net} is the net electric power generated measured in megawatts (MJ/s).

In the electric power industry, energy efficiency is frequently expressed as heat rate, HR, defined as:

$$\text{HR} = \frac{\dot{Q}}{P} \quad \text{(Btu/kW-h)} \tag{2.41}$$

where $\dot{Q}$ is the thermal energy input measured in English units (Btu/h) and P is the net electrical power output measured in SI units (kW). Heat rate is the reciprocal of thermodynamic efficiency except that it is expressed in mixed systems of units. Notice that low heat rates correspond to high thermodynamic efficiencies.

2.3.2 Energy Return on Energy Invested

Another way of tracking energy borrows from the economic concept of return on investment (ROI), which considers the amount of money invested in a project to the net amount of money returned over the course of the project (see Chapter 12). Applied to extractive energy resources, such as petroleum, natural gas, or coal, the so-called energy return on energy invested (EROEI) is the ratio of useful energy, E_{useful}, to the process energy expended in extracting the resource, $E_{process}$:

$$\text{EROEI} = \frac{E_{useful}}{E_{process}} \tag{2.42}$$

Of course, the amount of energy contained in fossil resources is much greater than the amount of energy required to pump it or dig it out of the ground and EROEI in this case is much greater than unity, ranging as high as 50 but more typically on the order of 5–20. Much the same can be said of harvesting biomass resources.

EROEI is less useful when considering the conversion of fossil or renewable resources into finished energy products. This is particularly true in comparing transportation fuels derived from petroleum and biomass, where EROEI may be greater than 10 for petroleum-derived gasoline and less than 2 for biofuels. Sometimes it is argued that this large disparity is a barrier to the use of biomass in the production of fuels. Certainly, it is true that biomass requires more extensive processing than petroleum to produce fuels, as described in subsequent chapters. Petroleum is the product of natural "geothermal processing" of biomass deposited into geological deposits many millions of years ago to produce hydrocarbons, much of which requires relatively little additional processing to yield transportation fuels.

However, the main reason for the large difference in EROEI is that the operational definition of EROEI is mathematically unbounded. Since the denominator of Equation 2.42 ($E_{process}$) excludes the chemical enthalpy of the feedstock, it can become very small compared to the numerator (E_{useful}). Since dividing a very large number by a very small number can exaggerate comparisons, EROEI can give an exaggerated impression of the relative amounts of energy that can be extracted from different resources. Although EROEI can be useful for comparing energy costs for extracting different kinds of energy resources, energy efficiency should be employed when comparing the fraction of an energy resource that can be converted to finished energy products.

This becomes clear upon inspecting the simplified energy balance on the fuel production facility illustrated in Figure 2.4. Energy entering the facility is of two kinds: $E_{feedstock}$ is the chemical enthalpy of the feedstock, while $E_{process}$ is the heat and power used to process the feedstock. Energy exiting the plant is of two kinds as well: E_{useful} is the useful energy produced, while E_{waste} is the incompletely converted feedstock and waste heat. As indicated in Table 2.2, the conversion of petroleum to gasoline has an EROEI of 10–20, while energy efficiency is 0.69–0.72. The conversion of corn grain to ethanol has an EROEI of 1.3, while energy efficiency is 0.35. Petroleum to gasoline is more favorable by both energy metrics, but EROEI greatly exaggerates this advantage. The EROEI simply indicates that eight times more energy must be expended to produce ethanol than gasoline, but the amount of energy recovered from petroleum compared to corn grain by these two processes differs by a more modest factor of 2.

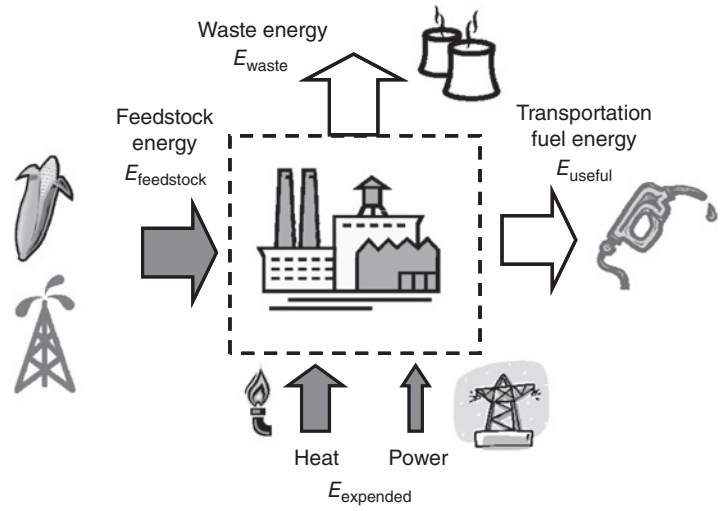

FIG. 2.4 Energy balance comparing conversion of petroleum to gasoline and corn grain to ethanol.

Table 2.2 Comparison of EROEI and energy efficiency for conversion of petroleum into gasoline and corn grain into ethanol

	Formula	Petroleum to Gasoline	Corn Grain to Ethanol
EROEI	$\text{EROEI} = \dfrac{E_{\text{useful}}}{E_{\text{expended}}}$	10–20	1.3
Energy efficiency	$\eta = \dfrac{E_{\text{useful}}}{E_{\text{expended}} + E_{\text{feedstock}}}$	0.69–0.72	0.35

The frequent misuse of EROEI may be responsible for the common misperception among many people that "you should get more energy out than you put in to fuels production." Certainly, we should expect the useful energy produced to be greater than the process energy input (EROEI > 1). However, when considering the total energy into a process ($E_{\text{feedstock}}+E_{\text{process}}$), one should expect to get less energy out in the form of fuels than one puts in. This is because for all real energy conversion processes, some energy is dissipated as heat or diverted to co-products other than the desired energy products with the result that the useful energy out is less than the total energy into the process.

2.3.3 Exothermic vs Endothermic Reactions in the Manufacture of Energy Products

The useful energy obtained from a process is always smaller than the energy expended, which is a consequence of the First and Second Laws of Thermodynamics. By way of analogy, a dropped rubber ball may be expected to recover some of its original elevation (gravitational potential energy) on the rebound, but no one seriously expects it to bounce higher than the height from which it was dropped. Similarly, the energy in fuel products will always be less than the energy inputs to the process.

What matters is preserving within the energy products as much as possible of the feedstock and processing energy used to manufacture the energy products, subject to the constraints of the laws of thermodynamics and the cost of accomplishing this purpose. Success in this endeavor is strongly dependent upon the nature of the energy source, the quality of the energy products, and the capital investment that can be economically justified. Figure 2.5 illustrates the efficiency of various energy conversion processes as the rebound of a dropped ball.

If a molecule is to serve as an energy product, clearly it must be able to undergo an energy releasing (exothermic) reaction within an engine or fuel cell. Conversely, we might expect that an energy absorbing (endothermic) reaction is required to manufacture an energy product. For example, the decomposition of water to produce hydrogen (along with oxygen) is an endothermic reaction. The energy to produce this energy product comes from an energy resource; for example, solar

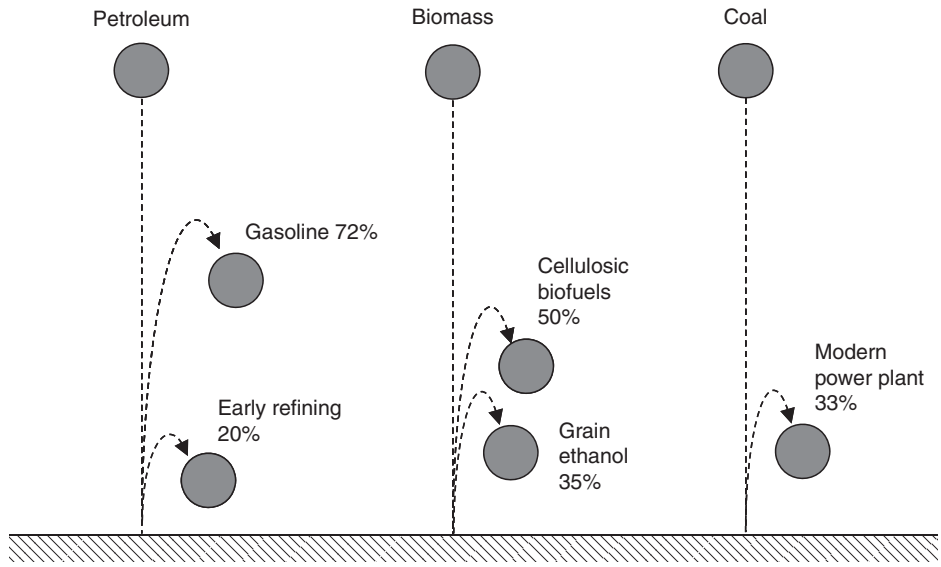

FIG. 2.5 Rebound of a dropped ball as an analogy for energy efficiency.

energy converted to electricity can then power an electrolysis unit to decompose water into hydrogen and oxygen.

In fact, both endothermic and exothermic reactions can be used to generate energy products. Consider an energy source that stores a large amount of chemical energy but in a form not convenient as transportation fuel. An exothermic reaction that rearranges chemical bonds to yield molecules more useful as transportation fuel might be employed despite the loss of part of the original energy. An example is fermentation of glucose to ethanol by yeast, an exothermic process that consumes about 3% of the chemical energy of the sugar to support the metabolism of the microorganism. From the standpoint of meeting the energy needs of the microorganism, fermentation is an appallingly inefficient process. However, the rejected energy is in the form of ethanol, an energy-dense liquid that is more convenient as transportation fuel than the sugar or starch granules from which it was produced.

Although exothermic reactions are commonly employed to convert energy resources into energy products, they are inherently less efficient than endothermic reactions for the production of energy products. This is because the energy released during the manufacture of energy products is frequently dissipated as waste heat. Nevertheless, many people have the misconception that the addition of energy to manufacture an energy product inevitably translates into low energy efficiency, which overlooks the fact that often this added energy is incorporated into the energy product. Fuel manufacture is usually a combination of exothermic and endothermic processes, which are ideally balanced to achieve the highest energy efficiency (i.e., very little waste energy is rejected from the process).

2.4 Chemical Equilibrium

A reaction is in chemical equilibrium when the reverse reaction rate balances the forward reaction rate. The two thermodynamic properties important in understanding chemical equilibrium are entropy $\bar{s}(T, p)$ and the Gibbs function $\bar{g}(T, p)$, also known as the Gibbs free energy. These properties are functions of both temperature and pressure. For an ideal gas, entropy is calculated by the expression:

$$\bar{s}_i(T, p) = \bar{s}_i^o(T) - \bar{R}\ln\frac{p_i}{p_{\text{REF}}} \tag{2.43}$$

where $\bar{s}_i^o(T)$ is the entropy of chemical species i at temperature T and reference pressure p_{REF} and $\bar{R}$ is the ideal gas constant. The Gibbs function can be calculated from its enthalpy and entropy:

$$\begin{aligned}\bar{g}_i(T, p) &= \bar{h}_i(T) - T\bar{s}_i(T, p) = \bar{h}_i(T) - T\left[\bar{s}_i^o(T) - \bar{R}\ln\left(\frac{p_i}{p_{\text{REF}}}\right)\right] \\ &= \left[\bar{h}_i(T) - T\bar{s}_i^o(T)\right] - \bar{R}\ln\left(\frac{p_i}{p_{\text{REF}}}\right) = \bar{g}_i^o - \bar{R}\ln\left(\frac{p_i}{p_{\text{REF}}}\right)\end{aligned} \tag{2.44}$$

When calculating the Gibb's function of chemically reacting systems, recall that the molar enthalpy $\bar{h}_i(T)$ includes both enthalpy of formation and sensible enthalpy change with respect to temperature (see Equation 2.38). Values of $\bar{s}_i^o(T)$ are tabulated in Table 2.1 for various gases with the reference pressure taken to be 1 atm. Notice that $\bar{g}_i^o(T)$ is the Gibb's function at temperature T and the reference pressure p_{REF}. It also sometimes tabulated but has not been included in Table 2.1, because it can be calculated from tabulations of $\bar{h}_i(T)$ and $\bar{s}_i^o(T)$.

Changes in these properties for a chemical reaction can be calculated in a manner similar to calculating changes in enthalpy:

$$\Delta S = \sum_{\text{p}} n_{\text{p}}\bar{s}_{\text{p}} - \sum_{\text{r}} n_{\text{r}}\bar{s}_{\text{r}} \tag{2.45}$$

$$\Delta G = \sum_{\text{p}} n_{\text{p}}\bar{g}_{\text{p}} - \sum_{\text{r}} n_{\text{r}}\bar{g}_{\text{r}} \tag{2.46}$$

These two properties are related by the following equation:

$$\Delta G = \Delta H - T\Delta S \tag{2.47}$$

where the temperature T is evaluated in Kelvin.

The Gibbs function is particularly useful in chemical thermodynamics. For example, the change in Gibbs function represents the maximum work that could

be produced from a chemically reacting system. As evident from Equation 2.47, the Gibbs function represents some fraction of the chemical enthalpy associated with a chemical reaction, dependent on the entropy and the temperature of the reaction, an important consideration in the discussion of fuel cells in Chapter 6.

The Gibbs function is also useful in calculating the equilibrium composition of a chemically reacting system. From the Second Law of Thermodynamics, it can be shown that chemical equilibrium for a constant pressure, constant temperature process corresponds to a minimum in the Gibbs function for the reaction. Although numerical methods are often employed to find this minimum for complex chemical reaction systems, the concept of equilibrium constant was developed for simpler reaction systems.

We consider the calculation of chemical equilibrium from equilibrium coefficients for a single reaction described by the stoichiometrically balanced equation:

$$\sum_{\mathrm{r}} \nu_{\mathrm{r}} A_{\mathrm{r}} = \sum_{\mathrm{p}} \nu_{\mathrm{p}} A_{\mathrm{p}} \tag{2.48}$$

where A_{r} and A_{p} are the symbols for the p-th chemical product and r-th chemical reactant, respectively, and ν_{r} and ν_{p} are their corresponding stoichiometric coefficients. For example, the stoichiometrically balanced reaction of hydrogen and oxygen to produce water is:

$$\mathrm{H_2} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{H_2O}$$

The stoichiometric coefficients for the reactants hydrogen and oxygen are 1 and $\frac{1}{2}$, respectively, and the stoichiometric coefficient for the product water is 1.

It can be shown that for ideal gas mixtures, products and reactants at chemical equilibrium conform to the relationship:

$$K_p(T) = \frac{\prod_{\mathrm{p}} \left(\frac{p_{\mathrm{p}}}{p_{\mathrm{ref}}}\right)^{\nu_{\mathrm{p}}}}{\prod_{\mathrm{r}} \left(\frac{p_{\mathrm{r}}}{p_{\mathrm{ref}}}\right)^{\nu_{\mathrm{r}}}} \tag{2.49}$$

where p_{p} and p_{r} are the partial pressure and stoichiometric coefficient of the p-th chemical product and r-th chemical reactant, respectively, and $K_p(T)$ is the equilibrium constant in terms of partial pressure as a function of temperature T. The symbol Π is mathematical shorthand that indicates the calculation of the product among the partial pressure terms of the chemical products or reactants.

The equilibrium constant is defined by the expression:

$$\ln\ K_p(T) = -\frac{\Delta G^{\mathrm{o}}}{\bar{R}T} \tag{2.50}$$

where ΔG^{o} is the Gibb's function for the stoichiometrically balanced chemical reaction of Equation 2.48:

$$\Delta G^{o} = \sum_{p} \nu_{p} \bar{g}_{p}^{o} - \sum_{r} \nu_{r} \bar{g}_{r}^{o} \tag{2.51}$$

The superscripts on the Gibbs functions indicate that they are evaluated at the reference pressure and the indicated temperature. However, the Gibb's function can also be calculated from the enthalpies and entropies at the reference pressure:

$$\Delta G^{o} = \sum_{p} \nu_{p} \left(\bar{h}_{p} - T\bar{s}_{p}^{o} \right) - \sum_{r} \nu_{r} \left(\bar{h}_{r} - T\bar{s}_{r}^{o} \right) \tag{2.52}$$

Example: The water–gas shift reaction is important during gasification, influencing the relative proportions of carbon monoxide (CO) and hydrogen (H_2) in the product gas:

$$CO + H_2O \rightarrow CO_2 + H_2$$

Assuming that the starting composition of a gas stream contains 1 kilomole each of CO, CO_2, H_2, and steam (H_2O) reacting at 10 atm pressure and 727°C (1000 K), what is the expected equilibrium composition of the gas mixture?

The first step is to write the overall molar balance for the conversion of the gases making up the initial gas mixture into an equilibrium mixture of the gases:

$$CO + CO_2 + H_2 + H_2O \rightarrow wCO + xCO_2 + yH_2 + zH_2O$$

From the above equation, molar balances on carbon, oxygen, and hydrogen can be performed:

carbon: $1 + 1 = w + x$

hydrogen: $2(1) + 2(1) = 2y + 2z$

oxygen: $1 + 2(1) + 1 = w + 2x + z$

These three equations are solved simultaneously in terms of one of the four variables, which is arbitrarily chosen here to be x. Substituting the solutions into the overall molar balance:

$$CO + CO_2 + H_2 + H_2O \rightarrow (2 - x)CO + xCO_2 + xH_2 + (2 - x)H_2O$$

Notice that for this particular reaction, the total number of moles is conserved (moles of reactants equal moles of products), although that is not necessarily the case for other reactions:

$$\sum_{\mathrm{r}} n_{\mathrm{r}} = n_{\mathrm{CO}} + n_{\mathrm{CO_2}} + n_{\mathrm{H_2}} + n_{\mathrm{H_2O}} = 1 + 1 + 1 + 1 = 4$$

$$\sum_{\mathrm{p}} n_{\mathrm{p}} = n_{\mathrm{CO}} + n_{\mathrm{CO_2}} + n_{\mathrm{H_2}} + n_{\mathrm{H_2O}} = (2 - x) + x + x + (2 - x) = 4$$

From the molar balances, the partial pressures of the products and reactants needed to solve Equation 2.49 can be calculated (in atmospheres of pressure):

$$p_{\mathrm{CO}} = x_{\mathrm{CO}} p = \frac{n_{\mathrm{CO}}}{n} p = \frac{(2 - x)}{4} 10\,; \quad p_{\mathrm{CO_2}} = x_{\mathrm{CO_2}} p = \frac{n_{\mathrm{CO_2}}}{n} p = \left(\frac{x}{4}\right) 10$$

$$p_{\mathrm{H_2}} = x_{\mathrm{H_2}} p = \frac{n_{\mathrm{H_2}}}{n} p = \left(\frac{x}{4}\right) 10; \qquad p_{\mathrm{H_2O}} = x_{\mathrm{H_2O}} p = \frac{n_{\mathrm{H_2O}}}{n} p = \frac{2 - x}{4} 10$$

Note that total moles, n, of chemical compounds are conserved in this example, although this is not generally the case. If moles are not conserved, then n in the above denominators would not be a constant but rather a function of x.

Substituting these partial pressures into Equation 2.49 and using the appropriate stoichiometric coefficient for each of the chemical species (where reference pressure is 1 atm):

$$K_p(T) = \frac{\prod_{\mathrm{p}} \left(\frac{p_{\mathrm{p}}}{p_{\mathrm{REF}}}\right)^{\nu_{\mathrm{p}}}}{\prod_{\mathrm{r}} \left(\frac{p_{\mathrm{r}}}{p_{\mathrm{REF}}}\right)^{\nu_{\mathrm{r}}}} = \frac{\left(\frac{x}{4}10\right)^1 \left(\frac{x}{4}10\right)^1}{\left(\frac{2 - x}{4}10\right)^1 \left(\frac{2 - x}{4}10\right)^1} = \frac{x^2}{(2 - x)^2}$$

Notice that pressure does not affect this equi-molar reaction. This expression can be simplified:

$$\left(K_{\mathrm{p}} - 1\right) x^2 - 4K_{\mathrm{p}} x + 4K_{\mathrm{p}} = 0$$

All that remains is to determine the value of the equilibrium coefficient K_p at 1000 K. From Equation 2.50, this requires the calculation of the Gibb's function for the stoichiometrically balanced equation:

$$\mathrm{CO} + \mathrm{H_2O} \rightarrow \mathrm{CO_2} + \mathrm{H_2}$$

Some tabulations of thermodynamic properties include the Gibb's functions for chemical species although more commonly only enthalpy and entropy are tabulated. Substituting appropriate values from Table 2.1 into Equation 2.52:

$$\begin{aligned}
\Delta G^{\circ} &= \sum_{\mathrm{p}} \nu_{\mathrm{p}} \left(\bar{h}_{\mathrm{p}} - T\bar{s}^{\circ}_{\mathrm{p}}\right) - \sum_{\mathrm{r}} \nu_{\mathrm{r}} \left(\bar{h}_{\mathrm{r}} - T\bar{s}^{\circ}_{\mathrm{r}}\right) \\
&= \nu_{\mathrm{CO_2}} \left\{\left[\bar{h}_{\mathrm{f}} + \left(\bar{h}(T) - \bar{h}(T_{\mathrm{ref}})\right]_{\mathrm{CO_2}} - T\bar{s}^{\circ}_{\mathrm{CO_2}}\right\} \\
&\quad + \nu_{\mathrm{H_2}} \left\{\left[\bar{h}_{\mathrm{f}} + \left(\bar{h}(T) - \bar{h}(T_{\mathrm{ref}})\right]_{\mathrm{H_2}} - T\bar{s}^{\circ}_{\mathrm{H_2}}\right\} \\
&\quad - \nu_{\mathrm{CO}} \left\{\left[\bar{h}_{\mathrm{f}} + \left(\bar{h}(T) - \bar{h}(T_{\mathrm{ref}})\right]_{\mathrm{CO}} - T\bar{s}^{\circ}_{\mathrm{CO}}\right\} \\
&\quad - \nu_{\mathrm{H_2O}} \left\{\left[\bar{h}_{\mathrm{f}} + \left(\bar{h}(T) - \bar{h}(T_{\mathrm{ref}})\right]_{\mathrm{H_2O}} - T\bar{s}^{\circ}_{\mathrm{H_2O}}\right\} \\
&= 1\,\{[-393\,520 + (42\,769 - 9364)] - 1000 \times 269.22\} \\
&+ 1\,\{[0 + (29\,154 - 8468)] - 1000 \times 166.11\} \\
&- 1\,\{[-110\,530 + (30\,355 - 8669)] - 1000 \times 234.42\} \\
&- 1\,\{[-241\,820 + (35\,882 - 9904)] - 1000 \times 232.60\} \\
&= -629\,335 - 145\,424 + 323\,264 + 448\,442 \\
&= -3053\ \mathrm{kJ/kmol}
\end{aligned}$$

Substituting into Equation 2.50:

$$\ln\ K_p = -\frac{\Delta G^{\circ}}{\bar{R}T} = -\left(\frac{-3053\ \mathrm{kJ/kmol}}{8.314\ \mathrm{kJ/kmol\,K} \cdot 1000\ \mathrm{K}}\right) = 0.367$$

$$K_p = \exp(0.367) = 1.444$$

Substituting this into the previously developed equilibrium expression in terms of variable x:

$$\left(K_p - 1\right)x^2 - 4K_p x + 4K_p = 0$$

$$(1.444 - 1)x^2 - 4(1.444)x + 4(1.444) = 0$$

$$0.444x^2 - 5.776x + 5.776 = 0$$

$$x = 1.092\ \mathrm{kmol}$$

Thus, the final molar product distribution is:

$$0.908\ \mathrm{kmol\ CO} + 1.092\ \mathrm{kmol\ CO_2} + 1.092\ \mathrm{kmol\ H_2} + 0.908\ \mathrm{kmol\ H_2O}$$

Further Reading

Engineering Thermodynamics

Moran, M., and Shapiro, H. (2010) *Fundamentals of Engineering Thermodynamics*, 7th edn. New York: John Wiley & Sons, Inc.

Chemical Reaction Mass Balances

Schmidt, L.D., (ed.) (2005) *The Engineering of Chemical Reactions*, 2nd edn. Oxford: Oxford University Press.

Energy Return on Energy Invested

Hall, A.S. and Hansen, D., (eds) (2011) *Special Issue on New Studies in EROI (Energy Return on Investment) Sustainability,* Vol. 3.

CHAPTER
3

Organic Chemistry

3.1 Introduction

Organic chemistry provides the foundation for understanding the transformation of plant materials into biofuels and biobased products. This chapter provides an overview to the subject for readers who are not familiar with the topic or require a brief review. More detailed descriptions can be found in the references at the end of this chapter.

The original distinction between inorganic and organic compounds was their source in nature. Inorganic compounds were derived from mineral sources, whereas organic compounds were obtained from plants or animals. Advances in chemical synthesis since the eighteenth century have made obsolete these definitions: the vast majority of organic chemicals commercially produced today are made from petroleum. The common feature of organic compounds is a skeleton of carbon atoms that include lesser amounts of other atoms, especially hydrogen, oxygen, and nitrogen, but also sulfur, phosphorus, and halides.

The high chemical valence of carbon allows for complex structures and large numbers of organic compounds. These include compounds consisting of chains of carbon atoms, referred to as acyclic or aliphatic compounds, and compounds containing rings of carbon atoms, known as carbocyclic or simply cyclic compounds. Some of these rings contain at least one atom that is not carbon (known as heteroatoms). These compounds are called heterocyclic compounds. Carbocyclic compounds are further classified as either aromatic compounds, in which electrons are shared among atoms to produce a particularly stable ring, or alicyclic compounds, which includes all non-aromatic cyclic compounds.

3.2 Classification of Reactions

A variety of reactions can occur among organic compounds. *Addition* reactions occur when two reactants combine to give a single product. *Elimination* reactions

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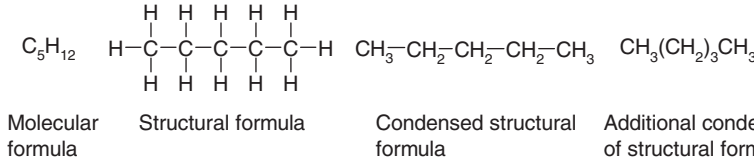
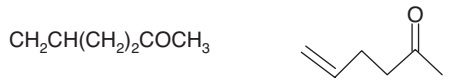
involve the splitting of a single compound into two compounds. Most elimination reactions form a product with a double bond containing the majority of the atoms found in the reactant. *Substitution* reactions involve replacement of one atom or group of atoms by a second atom or group of atoms. *Hydrolysis* is a particularly important instance of substitution reactions involving the action of water in splitting a large reactant molecule into two smaller product molecules. One product molecule is bonded to the hydrogen atom from the water, while the other product molecule is bonded to the hydroxyl group derived from the water. *Condensation* reactions involve two reactants combining to form one larger product with the simultaneous formation of a second, smaller product. Dehydration is a particularly important instance of condensation reactions in which water is the second, smaller product. Note that dehydration is the opposite of hydrolysis. *Rearrangement* reactions result from the reorganization of bonds within a single reactant to give an isomeric product.

3.3 Structural Formulas and Chemical Nomenclature

The molecular formula of a compound indicates its atomic composition. For example, the molecular formula for pentane is C_5H_{12}. Structural formulas show the arrangement of atoms and bonds. The number of lines between atoms in structural formulas indicates the number of bonds between them. For example, a carbon–hydrogen bond is represented by C–H, a carbon–carbon double bond is represented by C=C, and a carbon–carbon triple bond is written C≡C. Condensed structural formulas show only specific bonds; other bonds are left out but implied. The degree of condensation of structural formulas is somewhat arbitrary. Commonly, C–H bonds are not shown because they can only form single bonds. Additional condensation of structural formulas can be achieved by omitting C–C bonds.



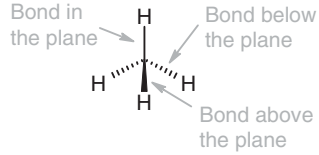
Bond-line structures are an extreme shorthand for representing molecules. Carbon atoms are omitted, but carbon–carbon bonds are illustrated in a zigzag arrangement. Carbon–hydrogen bonds are omitted, while bonds of carbon atoms to other atoms or molecular groups are shown explicitly.



Condensed structural formula

Bond-line structure

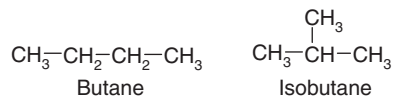
Sometimes it will be important to distinguish the three-dimensional structure of a molecule. In this case, perspective structural formulas are employed, with wedges indicating bonds that project out of the plane of the drawing. Solid wedges indicate bonds projecting above the plane of the drawing, while wedges shaded with parallel lines indicate bonds projecting below the plane of the drawing.



Perspective structural formula for methane

Organic compounds are named according to a system devised by the International Union of Pure and Applied Chemistry (IUPAC). The IUPAC name consists of three parts: prefix, parent, and suffix. The parent identifies the main carbon chain. The suffix identifies most of the functional groups present in the molecule. The prefix specifies the location of functional groups identified in the suffix as well as identifies some other atoms or groups of atoms attached to the main carbon chain. The nomenclature of organic compounds is further elaborated in the subsequent discussions on various functional groups. Many compounds continue to be known by their common names either because of long usage or to avoid the unwieldy nomenclature of some compounds derived from biological sources.

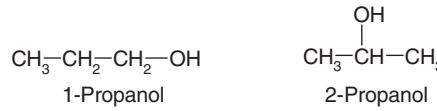
Compounds that have the same molecular formula but different structures are isomers. Isomers that differ in their carbon skeleton are called skeletal isomers. For example, butane and isobutane both have the molecular formula of C_4H_{10}, but butane is a straight-chain hydrocarbon, whereas isobutane includes a short side-chain.



Butane Isobutane

Isomers that have different functional groups are called functional group isomers. For example, the molecular formula C_2H_6O represents both ether, which has a functional group in the form of divalent oxygen, and an alcohol, which has a functional group in the form of monovalent hydroxyl group (OH).

Positional isomers have the same molecular formulas and functional groups. They differ only in the location of the functional groups in the carbon chains. For example, 1-propanol and 2-propanol are alcohols of molecular formula C_3H_7OH, but the former has its single hydroxyl group located at the end of the carbon chain, whereas the latter has its hydroxyl group at the middle of the chain.



3.4 Classification of Organic Compounds

Organic compounds are conveniently classified according to functional groups—the molecular structures that give the compounds distinctive chemical and physical properties. Those functional groups of particular interest to the chemistry of biobased products are summarized in Table 3.1. The rest of this section describes the chemistry of these functional groups.

3.4.1 Alkanes

The simplest organic compounds consist only of carbon and hydrogen atoms and are known as hydrocarbons. Hydrocarbons containing only carbon–carbon single bonds are classified as alkanes and conform to the general chemical formula of C_nH_{2n+2}. Alkanes are also called paraffins. A hydrocarbon that contains only carbon–carbon single bonds is said to be saturated.

Alkanes with a continuous chain of carbons atoms are normal alkanes. The names and molecular formulas for normal alkanes containing up to 10 carbon atoms are listed in Table 3.2. Note that all end in the suffix "-ane." The first four names are based on common names, while those with more than four carbon atoms are derived from Greek numbers that indicate the number of carbon atoms. Familiar alkanes include the fuels—methane (CH_4), propane (C_3H_8), and butane (C_4H_{10}). Gasoline is a mixture of higher boiling point alkanes.

A normal alkane molecule minus one hydrogen atom is known as an alkyl group; for example, "CH_3–" is the methyl group. As shown in Table 3.2, the names of the alkyl groups conform to the names of the corresponding alkanes. The short hand for an alkyl group is "R–" (i.e., "remainder of molecule"). The number of alkyl groups attached to hydrocarbons is a convenient way to classify them.

Branched alkanes result when carbon atoms in the chain bond to other carbon atoms, forming side chains. These still have the general formula C_nH_{2n+2} and thus

Table 3.1 Classification of organic compounds based on functional groups

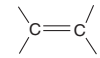
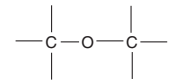
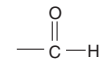
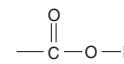
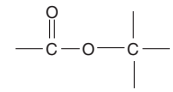
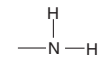
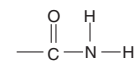
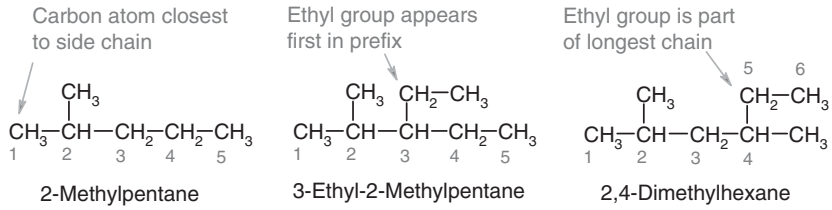
Class	General Formula	Functional Group	Suffix to Chemical Name
Alkane	RH		-ane
Alkene	$RCH{=}CH_2$ RCH=CHR $R_2C{=}CHR$ $R_2C{=}CR_2$		-ene
Alkyne	RC≡CH RC≡CR		-yne
Aromatic hydrocarbon	ArH		–
Alcohol or phenol	ROH		-ol
Ether	ROR		–
Aldehyde	RCHO		-al
Ketone	RCOR		-one
Carboxylic acid	RCOOH		-oic acid
Ester	RCOOR		-oate
Amine	RNH_2		-amine
Amide	$RCONH_2$		-amide

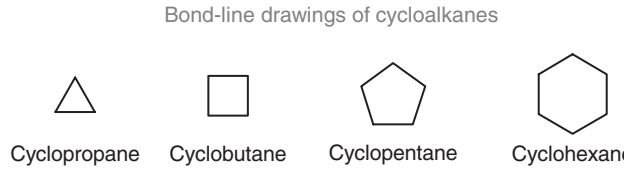
Table 3.2 Names of alkanes and alkyl groups

	Alkane		Alkyl Group	
Number of Carbon Atoms	Name	Molecular Formula	Name	Molecular Formula
1	Methane	CH_4	Methyl	$CH_3–$
2	Ethane	C_2H_6	Ethyl	$C_2H_5–$
3	Propane	C_3H_8	Propyl	$C_3H_7–$
4	Butane	C_4H_{10}	Butyl	$C_4H_9–$
5	Pentane	C_5H_{12}	Pentyl	$C_5H_{11}–$
6	Hexane	C_6H_{14}	Hexyl	$C_6H_{13}–$
7	Heptane	C_7H_{16}	Heptyl	$C_7H_{15}–$
8	Octane	C_8H_{18}	Octyl	$C_8H_{17}–$
9	Nontane	C_9H_{20}	Nontyl	$C_9H_{19}–$
10	Decane	$C_{10}H_{22}$	Dectyl	$C_{10}H_{21}–$

represent isomers of the normal alkanes. They are named such that the longest continuous chain is the parent part of the IUPAC name. The name and position of the alkyl groups making up the side chains are included in the suffix part of the IUPAC name. Positions of alkyl groups are specified by numbering carbon atoms along the main carbon chain, with the lowest numbered carbon atom appearing at the end of the chain closest to the first branch chain. The prefix specifies all alkyl groups attached to the main chain, with the prefixes listed alphabetically rather than by location on the main chain. Two or more groups of the same name are indicated by the prefix di-, tri-, tetra-, etc. For example, an alkane consisting of five carbon atoms in the main chain with a methyl group attached to the carbon atom second to the end of the main chain is called 2-methylpentane. Replacement of an ethyl group for one of the hydrogen atoms attached to the third carbon of 2-methylpentane is called 3-ethyl-2-methylpentane. Note that if the ethyl group had been attached to the fourth carbon atom, it would not be called 4-ethyl-2-methylpentane because the ethyl group now becomes part of the longest chain in the molecular structure. Instead, it should be considered as consisting of a six-carbon main chain with two methyl groups attached to the second and fourth carbon atoms, which is called 2,4-dimethylhexane.



Closely related to the alkanes are the cycloalkanes, which contain carbon–carbon single bonds in a ring structure and conform to the general chemical formula of C_nH_{2n}. The simplest cycloalkanes are cyclopropane (C_3H_6) in a triangular ring, cyclobutane (C_4H_8) in a rectangular ring, cyclopentane (C_5H_{10}) in a pentagonal ring, and cyclohexane (C_6H_{12}) in a hexagonal ring.

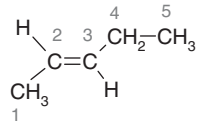


Because C–H bonds are nonpolar, alkanes are nonpolar, with implications for the physical properties of these hydrocarbons. Alkanes are not soluble in water, a highly polar compound (following the rule-of-thumb that "like dissolves like"). The absence of polarity also means that alkane molecules do not strongly interact; thus, boiling points of alkanes are relatively low compared to other organic

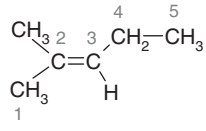
compounds, increasing with molecular weight. The C–C and C–H bonds of alkanes are not very reactive with the exception of oxidation. The high heats of oxidation make alkanes attractive as fuels.

3.4.2 Alkenes and Alkynes

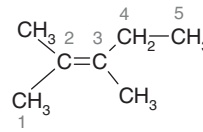
Hydrocarbons with carbon–carbon double bonds are called alkenes and conform to the general chemical formula of C_nH_{2n}. The IUPAC nomenclature follows that of the alkanes (see Table 3.2) except the suffix "-ene" is used instead of "-ane." Like alkanes, alkenes can have branched chains. The longest continuous chain containing the double bond is the parent. Carbon atoms are numbered consecutively from the end nearest to the double bond. Isomers are distinguished by including the number of the first carbon atom in the double bond in the prefix to the parent name. The prefix also specifies the type and location of all alkyl groups attached to the main chain, with the prefixes listed alphabetically rather than by location on the main chain. Two or more groups of the same name are indicated by the prefix di-, tri-, tetra-, etc.



2-Pentene



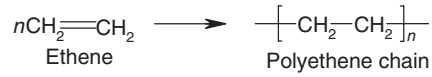
2-Methyl-2-Pentene



2,3-Dimethyl-2-Pentene

Common names are often employed in the chemical industry. For example, the simplest alkene, ethene (C_2H_4), is commonly known as ethylene. Ranked first among organic chemicals in annual production in the United States, ethene is produced from natural gas liquids.

Alkenes are widely used in the production of polymers, a high-molecular-weight compound created by the repetitive reaction of low-molecular-weight molecules, known as monomers, to form long carbon chains. Polymerization of alkenes occurs by addition reactions—carbon chains are lengthened by addition of monomers without the formation of other products. For example, ethene, at elevated pressures and temperatures and in the presence of a trace amount of oxidant, yields a polymeric chain of molecular mass of 50 000 to 300 000 known as polyethene (familiarly known as polyethylene), a low-density plastic used in the manufacture of plastic bags and squeeze bottles.

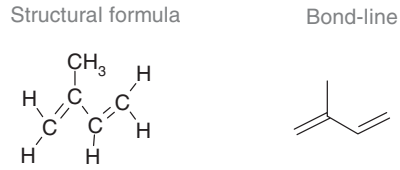


Ethene Polyethene chain

Other polymers from alkenes include polypropene, commonly called polypropylene and spun into fibers for carpets and ropes; polychloroethene, also known as

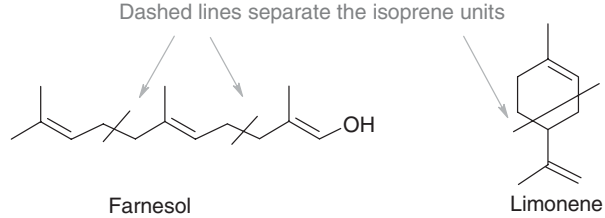
polyvinyl chloride, widely used in making both rigid plastic products, such as pipe and floor tiles, as well as flexible plastic products, such as shower curtains and garden hoses; polydichloroethene, used in plastic wrap; polytetrafluoroethene, the basis of Teflon; polyacrylonitrile, used in synthetic fibers; polystyrene, used in Styrofoam; and polymethyl methacrylate, used in Plexiglass.

If more than one double bond appears in a molecule, the location of each double bond is indicated in the prefix, and the suffix becomes -diene, -triene, -tetraene as appropriate to indicate the number of double bonds. Alkadienes, containing two double bonds, are commonly called dienes. If the two double bonds of a diene are separated by one single bond, the resulting compound, known as a conjugated diene, has chemical properties distinct from other alkenes (if separated by more than one single bond, the double bonds are unconjugated dienes and have properties similar to other alkenes). An important example of a conjugated diene is 2-methyl-1,3-butadiene, commonly known as isoprene.



2-Methyl-1,3-Butadiene (isoprene)

Isoprene is the basis for many important natural chemicals. Both terminal carbon atoms can bond with terminal carbon atoms of other isoprenes to form a variety of cyclic and acyclic compounds with different degrees of saturation and various functional groups attached. Terpenes, compounds of two or more isoprene units joined together with the generic formula $(C_5H_8)_n$, have distinctive odors and flavors. They are responsible for the fragrant odors of pine trees and the bright colors of tomatoes and carrots. Terpenes are classified by the number of isoprene units they contain—monoterpenes have two isoprene units, sesquiterpenes have three isoprene units, and diterpenes, triterpenes, and tetraterpenes contain four, six, and eight isoprene units, respectively. Examples include farnesol, an acyclic sesquiterpene first isolated from roses and citronella, and limonene, a cyclic monoterpene with a distinctive lemon odor.



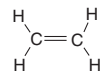
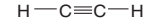
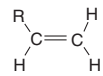
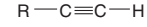
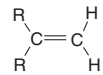
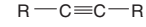
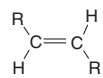
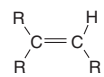
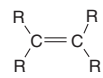
Farnesol Limonene

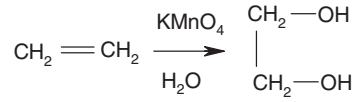
Hydrocarbons with carbon–carbon triple bonds are called alkynes and conform to the general chemical formula C_nH_{2n-2}. The nomenclature follows that of the alkanes (see Table 3.2) except the suffix "-yne" is used instead of "-ane," although common names are often employed in the chemical industry. For example, the simplest alkyne, ethyne (C_2H_2), is commonly known as acetylene, the fuel for many high-temperature cutting torches. Compounds with multiple triple bonds are diynes, triynes, and so on. Compounds with both double and triple bonds are called enynes; numbering of these compounds starts from the end nearest the first multiple bond.

The presence of double and triple bonds in alkenes and alkynes, respectively, makes them unsaturated hydrocarbons. These unsaturated compounds are often classified according to the number of alkyl groups (R–) attached to the double or triple bond unit, which is known as the "degree of substitution." As an example, various degrees of substitution are illustrated in Table 3.3 for an alkene and an alkyne.

Both alkenes and alkynes are nonpolar compounds with physical properties similar to those for alkanes. However, the double and triple bond components in alkenes and alkynes are weaker than the single bond in alkanes, making them more chemically reactive than alkanes. Unsaturated compounds are easily oxidized without destroying the carbon chain. For example, potassium permanganate readily oxidizes ethene to 1,2-ethanediol, commonly known as ethylene glycol, familiar as automotive anti-freeze.

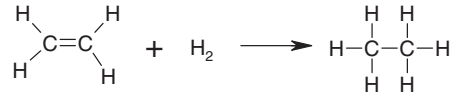
Table 3.3 Examples of substitutions of alkyl groups in alkenes and alkynes

Substitution	Ethene	Ethyne
Unsubstituted		
Mono-substituted		
Di-substituted		
Di-substituted		
Tri-substituted		
Tetra-substituted		



Ethene 1,2-Ethanediol

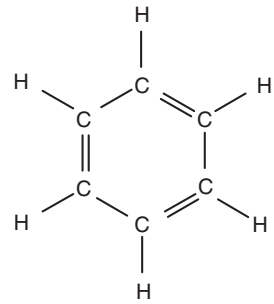
An important reduction reaction, known as hydrogenation, is the conversion of a C=C bond in an alkene or the C≡C bond in an alkyne to a C–C bond by the addition of hydrogen in the presence of a catalyst.

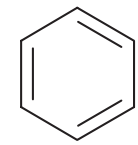


Ethene Ethane

3.4.3 Aromatic Compounds

Among the most important cyclic hydrocarbon structures is the benzene ring, consisting of six carbon atoms in an extremely stable hexagonal structure.



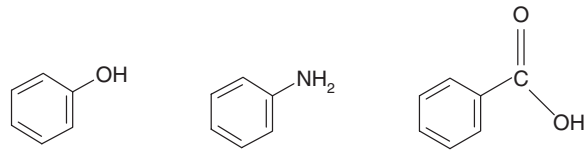


Benzene: structural formula Benzene: bond-line structure

This stability is the result of the sharing of electrons (delocalization) among all the atoms of the ring, a condition that can be predicted by the Hückel rule. Compounds that satisfy the Hückel rule are known as aromatic compounds because many of these compounds have distinctive fragrances, such as vanilla and oil of wintergreen. Compounds based on the six-carbon ring of benzene are not the only cyclic compounds classified as aromatic, but they are among the most important compounds in organic chemistry.

Substitution of various chains or ring structures for the hydrogen atoms yields a tremendous variety of chemical compounds with a range of useful properties. For example, substitution with a hydroxyl group yields phenol, a crystalline acidic compound used in the manufacture of phenolic resins and readily produced by the pyrolysis of biomass. Substitution with an amine group yields aniline, the basis of the synthetic dye industry in the nineteenth century. Substitution with a carboxylic

group yields benzoic acid, a white crystalline acid found naturally in cranberries and used especially as a preservative of foods.

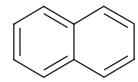


Phenol Aniline Benzoic acid

If one or more of the carbon atoms in the ring of an aromatic compound are substituted by another atom, usually nitrogen, sulfur, or oxygen, the resulting compound is said to be a heterocyclic aromatic compound. Examples include pyridine, a pungent, water-soluble flammable liquid that is the parent of many naturally occurring organic compounds, and furan, a five-member ring (unsaturated) ether obtained by dehydrating (removal of water) and decarbonylating (removal of carbon monoxide) carbohydrate obtained from woody or herbaceous biomass.

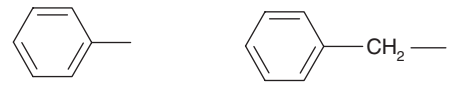
Pyridine Furan

Aromatic compounds consisting of two or more rings "fused" together are known as polycyclic aromatic hydrocarbons. These compounds are planar, that is, all atoms in the rings and those atoms directly attached to the rings are in a plane. A prominent example is naphthalene, often used in the manufacture of mothballs.



Naphthalene

An aromatic ring attached to a larger parent structure is an aryl group, often symbolized by "–Ar," just as the alkyl group is symbolized by R–. Examples of aryl groups derived from benzene are the phenyl group and the benzyl group.



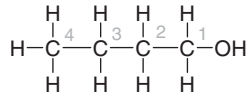
Phenyl group Benzyl group

3.4.4 Alcohols and Phenols

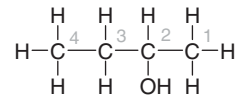
Hydrocarbons, compounds of only carbon and hydrogen, make up only a small fraction of plant material. Most plant material incorporate large amounts of oxygen and, thus, functional groups containing oxygen play important roles in the

chemistry of biobased products. Organic compounds that have functional groups containing oxygen include alcohols, phenols, ethers, aldehydes, ketones, acids, esters, and amides.

The hydroxyl group, "–OH," characterizes alcohol, which are named according to the longest carbon chain containing the hydroxyl group. The parent name is obtained by adding "-ol" to the name of the alkyl group attached to the hydroxyl group. The location of the hydroxyl group in the parent chain is specified by prefixing to the name a number corresponding to the carbon atom to which the hydroxyl group is attached. The lowest numbered carbon atom is the one at the end of the carbon chain that is located closest to the hydroxyl group. For example, an alcohol formed from the attachment of a hydroxyl group to the end of the butyl group is known as 1-butanol, whereas a hydroxyl group attached to the second of the four carbon atoms in the butyl group is called 2-butanol.

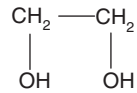


1-Butanol

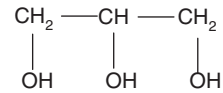


2-Butanol

Some alcohols, known as polyols, contain two or more hydroxyl groups. They are named by retaining the "-e" in the name of the parent alkane and adding -diol, -triol, and so forth to indicate the number of hydroxyl groups attached, although many polyols have common names. For example, 1,2-ethanediol consists of two hydroxyl groups attached to an ethane background. Commonly known as ethylene glycol, it is used both as anti-freeze and as an important chemical in the manufacture of the synthetic fiber Dacron® and Mylar® film. An example of a triol is 1,2,3-propanetriol, which consists of three hydroxyl groups attached to a propane chain. Commonly known as glycerol, it is the backbone of fats and oils.

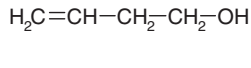


1,2-Ethanediol

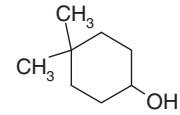


1,2,3-Propanetriol

Alcohols are also formed by attaching hydroxyl groups to ring structures and carbon chains containing double or triple bonds. The carbon atoms on ring structures are numbered starting with the carbon atom attached to the hydroxyl group and continuing around the ring in the direction that gives the lowest numbers to atoms attached to substituents. Alcohols containing double and triple bonds are named by including a prefix number that labels the position of the double bond and a suffix that combines the position of the hydroxyl group along with the designation -ol.



3-Buten-1-ol

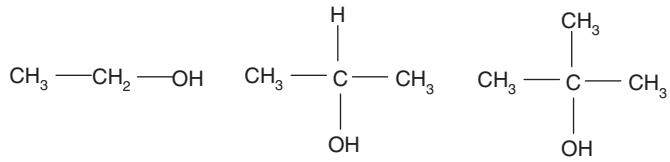


4,4-Dimethyl-Cyclohexanol

The hydroxyl group is responsible for several prominent physical properties of alcohols. The hydroxyl group serves as both a hydrogen bond donor and a hydrogen bond acceptor, resulting in large intermolecular forces between alcohol molecules. The large energy required to separate these bonds is responsible for high boiling points of alcohols compared to alkanes of similar molecular weight. Like water, lower-molecular-weight alcohols are highly polar, resulting in high solubility in water and polar organic compounds.

Alcohols can serve as both proton donors and proton acceptors. When an alcohol loses a proton, a conjugate base called an alkoxide ion, $R–O^-$, is produced. Alcohols are very weak acids. When an alcohol accepts a proton, a conjugate acid called an oxonium ion, $R–OH_2^+$, is produced. Alcohols are very weak bases, forming only under the action of a very strong acid.

Alcohols are classified as primary, secondary, or tertiary alcohols depending upon how many carbon atoms are attached to the carbon atom that is bonded to the hydroxyl group.

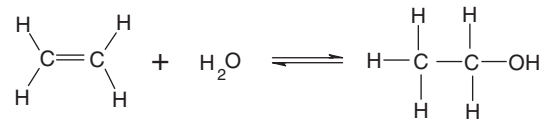


Primary alcohol Secondary alcohol Tertiary alcohol

Removal of a water molecule from an alcohol is a dehydration reaction, which is an example of an elimination reaction. This reaction requires an acid catalyst, such as sulfuric acid or phosphoric acid, and is illustrated by the formation of ethylene from ethanol.

Primary alcohols, which have the general formula of RCH_2OH, can be oxidized to aldehydes, a class of organic compounds with the general formula of RCHO; the reaction is accompanied by the removal of two hydrogen atoms. The resulting aldehydes can be further oxidized to carboxylic acids, a class of organic compounds with the general formula of RCOOH; the oxidized molecule gains an oxygen atom. Secondary alcohols, which have the general formula of R_2CHOH, are oxidized to ketones, a class of organic compounds with the general formula of RCOR, which cannot be further oxidized because there is no hydrogen atom on the oxygen bearing carbon atom of the ketone. Tertiary alcohols, which have the general formula R_3COH, cannot be readily oxidized because the carbon atom bearing the hydroxyl group has no hydrogen atom.

Alcohols can be synthesized from alkenes by hydration (addition of water). Conversely, alkenes can be dehydrated (removal of water) to form alcohols. For example, the equilibrium expression for hydration of ethene and dehydration of ethanol is given by

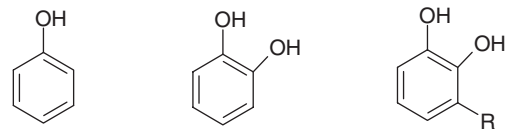


Ethene Ethanol

The direction of the reaction is controlled by Le Chatelier's principle. Thus, excess water will drive the reaction toward alcohol formation, whereas a deficiency in water will drive the reaction toward alkene formation. This latter condition is achieved by reaction in concentrated sulfuric acid, where water concentration is very low.

The attachment of a hydroxyl group to benzene forms an important class of compounds known as phenols. Both alcohols and phenols can be considered organic analogs of water and undergo reactions that are similar to water, such as reaction with alkali metals to form hydrogen gas. However, the delocalization of electrons in the benzene ring makes the C–O bond in phenols much stronger than the C–O bond in alcohols, resulting in important chemical differences between these two classes of compounds. In alcohols, the hydroxyl group is readily displaced, whereas the strong C–O bond in phenol prevents this from occurring except under extreme conditions.

Examples of phenolic compounds include phenol with one hydroxyl group attached to the benzene ring; pyrocatechol, containing two adjacent hydroxyl groups and originally obtained from pyrolysis of biomass; and urushiols, a mixture of pyrocatechol derivatives with saturated and unsaturated side chains of 15 or 17 carbon atoms, which is the oily irritant in poison ivy. Phenol is used to manufacture epoxy resins and polymers such as Bakelite and nylon. It is also used in the manufacture of dyes, herbicides, and disinfectants.

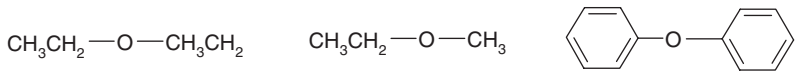


Phenol Pyrocatechol Generic urushiol

3.4.5 Ethers

Ethers contain two groups, which may be alkyl or aryl groups, bonded to an oxygen atom. The smaller alkyl group and the oxygen atom constitute an alkoxy

group (R–O). Similarly, an aryl group and the oxygen atom constitute a phenoxy group (Ar–O). The alkoxy and phenoxy groups are considered substituents on the larger parent alkyl or aryl group. These groups can form either symmetrical ethers or unsymmetrical ethers, depending upon whether the same or different alkyl or aryl groups are attached to the two oxygen bonds. Ethers are named by listing the alkyl or aryl groups in alphabetical order and appending the name ether.



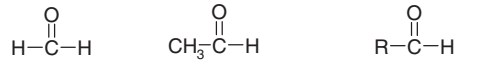
Diethyl ether (symmetrical ether) | Ethyl methyl ether (asymmetrical ether) | Diphenyl ether (symmetrial ether)

The two C–O bonds result in substantial dipole moments for ethers. They are more polar than alkanes but less polar than alcohols. Thus, they are more soluble in water than alkanes of similar molecular weight. This functional group has no hydrogen bond donors; thus, boiling points are substantially less than for alcohols of comparable molecular weight and similar to alkanes of comparable molecular weight. Ethers are stable compounds that do not react with most common reagents. Ethers have found applications as solvents and anesthetics.

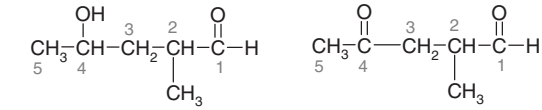
3.4.6 Aldehydes and Ketones (Carbonyl Compounds)

Aldehydes and ketones are characterized by the carbonyl functional group, which consists of an oxygen atom double-bonded to carbon (C=0). The carbon atom of the carbonyl group is called the carbonyl carbon atom, and the oxygen atom is called the carbonyl oxygen atom. The carbonyl group is prevalent in compounds isolated from plants. Aldehydes and ketones, collectively known as carbonyl compounds, often have pleasant odors and are responsible for the fragrant smell of flowers. At one time, plants were the sole source of aldehydes and ketones used in such products as perfumes.

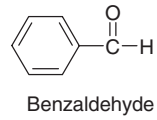
An aldehyde is a carbonyl group with the carbonyl carbon atom bonded to a hydrogen atom and either another hydrogen atom or an alkyl or aryl group. The aldehydes are named by addition of the suffix "-al" to the root alkyl name corresponding to the longest continuous carbon chain containing the carbonyl group. For example, methanal is a carbonyl group (C=O) bonded to two hydrogen atoms. Methanal is more commonly known as formaldehyde, a preservative for biological specimens. Ethanal, containing two carbon atoms, consists of a carbonyl group bonded to one hydrogen atom and one methyl group (CH_3). Ethanal is more commonly known as acetaldehyde, a compound found in a variety of fruits and vegetables.



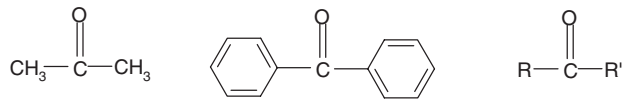
The alkyl group attached to the carbonyl group may also have side chains, which must be indicated in the name. This is done by specifying the location and type of alkyl group as a prefix to the parent name. Carbon atoms in the parent chain are numbered starting with the carbonyl carbon atom. The presence of carbonyl side chains (C=O) is designated with the prefix "oxo-."



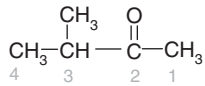
An example of an aldehyde incorporating an aryl group is benzaldehyde, consisting of a carbonyl group bonded to a hydrogen atom and a phenyl group (i.e., a benzene ring). Benzaldehyde is known as oil of almonds and used in flavorings and perfumes.



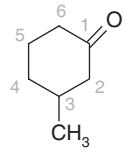
When the carbonyl carbon atom is bonded to two other carbon atoms, the compound is known as a ketone. These other carbon atoms can be part of either an alkyl group or an aryl group. The ketones are named by addition of the suffix "-one" to the root alkyl name corresponding to the longest continuous carbon chain containing the carbonyl group. Replacing the hydrogen bond in ethanal, for example, with another methyl group yields the solvent propanone (commonly known as acetone), while replacing the hydrogen bond in benzaldehyde with another phenyl group yields benzophenone, a component in the manufacture of perfumes and sunscreens.



For more complicated ketones, the location of the carbonyl carbon atom and the position and type of side chains must be specified. The carbon atoms are numbered from the end of the parent chain closest to the carbonyl carbon atom. Cyclic ketones are called cycloalkanones. The carbonyl carbon atom is designated as the first carbon atom in the ring.



3-Methyl-2-Butanone

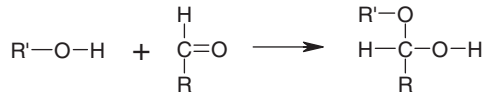


3-Methylcyclohexanone

The carbonyl group is polar; thus, carbonyl compounds have boiling points that are higher than alkanes of similar molecular weight. The carbonyl group cannot act as a hydrogen donor, but the carbonyl oxygen atom can serve as a hydrogen acceptor, allowing aldehydes and ketones to form hydrogen bonds with water. Accordingly, lower-molecular-weight compounds containing the carbonyl group are miscible in water. For the same reason, alcohols and carboxylic acids are soluble in these compounds. Several ketones are excellent solvents for polar organic compounds.

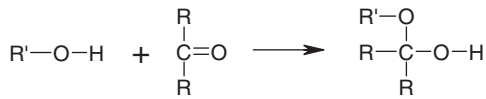
Aldehydes can be synthesized by the controlled oxidation of primary alcohols, while ketones can be prepared by oxidation of secondary alcohols. Carbonyl compounds can participate in a variety of chemical reactions including oxidation to carboxylic acids, reduction to alcohols, and condensation to give a group of compounds known as aldols, which contain both aldehyde and alcohol functional groups. They also participate in acid-catalyzed addition reactions with alcohol to form compounds very important to carbohydrate chemistry.

In the addition reaction of alcohol with a carbonyl compound, the hydrogen atom from the hydroxyl group of the alcohol adds to the carbonyl oxygen atom, whereas the remaining "–R" fragment from the alcohol, known as the alkoxy group, adds to the carbonyl carbon atom. The product is called hemiacetal if the carbonyl compound in the reactants is aldehyde.



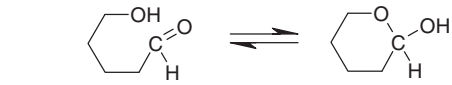
Alcohol Aldehyde Hemiacetal

The product is called hemiketal if the carbonyl compound in the reactants is ketone.



Alcohol Ketone Hemiketal

The equilibrium constant for the formation of either hemiacetal or hemiketal is less than 1; thus, these compounds are usually unstable. However, if the hydroxyl and carbonyl groups are part of the same molecule, a stable cyclic product forms.

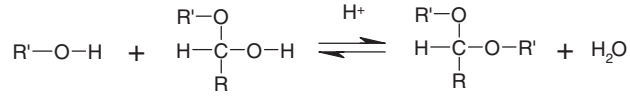


Hydroxyl and carbonyl groups in same organic compound

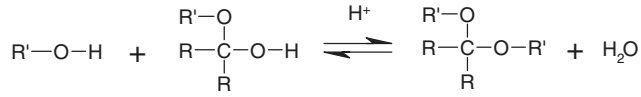
Stable cyclic hemiacetal or hemiketal product

Carbohydrates contain both hydroxyl and carbonyl groups and commonly form such cyclic hemiacetals or hemiketals, as will be discussed in a later section.

Note that the resulting hemiacetal or hemiketal contains a new hydroxyl group. In an acidic solution, this hydroxyl group can be replaced by another alkoxy group derived from alcohol to form acetal and ketal, respectively.



Alcohol Hemiacetal Acetal

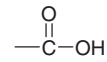


Alcohol Hemiketal Ketal

The position of the equilibrium can be shifted toward formation of acetal or ketal by adding alcohol or removing water from the reaction. Note that the reverse reactions are acid-catalyzed hydrolysis of acetal or ketal to form carbonyl compounds and alcohol. Cyclic hemiacetyls and cyclic hemiketals react with alcohols to form cyclic acetals and cyclic ketals, respectively.

3.4.7 Carboxylic Acids

The carboxyl group, a combination of carbonyl group and hydroxyl group, characterizes carboxylic acids.

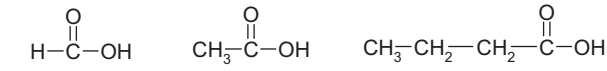


Carboxyl group

The carbonyl group and hydroxyl group modify the behavior of each other; thus, the behavior of carboxylic acids differs from that of carbonyl compounds and alcohols.

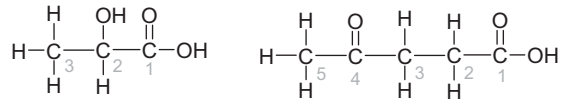
Carboxylic acids are named by replacing the "-e" in the root alkyl name corresponding to the longest continuous carbon chain containing the carboxyl group. For example, attached to a hydrogen atom, it forms methanoic acid, commonly known as formic acid, a pungent liquid secreted by ants when disturbed; attached to the methyl group, it forms ethanoic acid, commonly known as acetic acid, the main ingredient of vinegar and important in the manufacture of polymers;

attached to the propyl group, it forms butanoic acid, commonly known as butyric acid, responsible for the unpleasant odor of rancid butter and rotting hay.



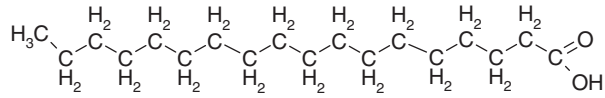
Methanoic acid Ethanoic acid Butanoic acid

Carboxylic acids can have additional functional groups attached to the carbon chain; these are named by adding prefixes that indicate the position of the functional group. The carbonyl carbon atom at the end of the parent chain is designated as the first carbon atom. Examples include 2-hydroxypropanoic acid, commonly known as lactic acid, important in the manufacture of biodegradable plastics, and 4-oxopentanoic acid, commonly known as levulinic acid, which can be used as a fuel additive or in the production of synthetic resins and plastics.

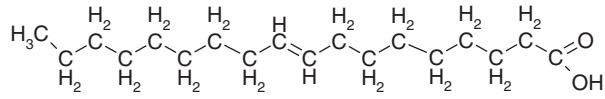


2-Hydroxypropanoic acid 4-Oxopentanoic acid

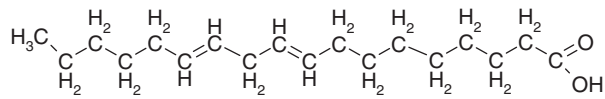
A special class of carboxylic acids, known as fatty acids, consists of long carbon chains with even numbers of carbon atoms. Fatty acids differ primarily in chain length and degree of saturation. Chains are generally linear and most commonly are 16 or 18 carbons long. They may be saturated, like stearic acid; monounsaturated (containing one carbon–carbon double bond), like oleic acid; or polyunsaturated (containing several carbon–carbon double bonds), like linoleic acid. These are important components of fats and oils.



Stearic acid

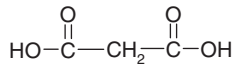


Oleic acid

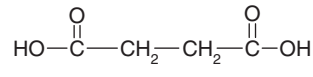


Linoleic acid

Carboxylic acids containing a –COOH group at each end of the carbon chain are known as dicarboxylic acids or simply diacids. They are named by adding -dioic acid to the end of the alkyl root name. Examples include propanedioc acid, commonly known as malonic acid, and butanedioic acid, commonly known as succinic acid, both of which are being proposed as precursors in the synthesis of biobased polymers.



Propanedioc acid

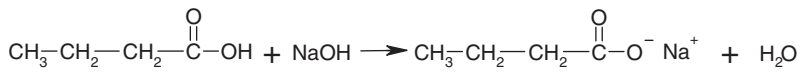


Butanedioic acid

The boiling points of carboxylic acids are high because the formation of hydrogen-bonded dimers causes the molecules to interact very strongly. Carboxylic acids serve both as hydrogen bond donors and as hydrogen bond acceptors; thus, carboxylic acids are soluble in water. Liquid carboxylic acids have sharp, unpleasant odors.

The carboxyl group readily serves as a proton donor; thus, carboxylic acids are relatively strong acids compared to alcohols, able to react with some metals to liberate hydrogen and react with metallic carbonates to liberate carbon dioxide, but they are rather weak acids compared to mineral acids.

The reaction of carboxylic acid with a base yields the conjugate base $RCOO^-$ known as the carboxylate ion, which is named by replacing the -oic acid ending with -oate. The salt of a carboxylic acid is named by preceding the name of the carboxylate ion by the name of the metal ion.



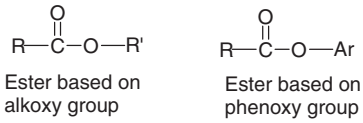
Butanoic acid Sodium butanoate

Because they are ionic, carboxylates are more soluble than their corresponding carboxylic acids. This feature is often used to separate carboxylic acids from other nonpolar organic compounds.

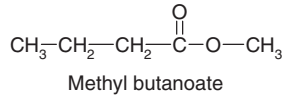
3.4.8 Esters

The RCO unit in a carboxylic acid is called an acyl group. A number of carboxylic acid derivatives result by replacing the hydroxyl group that is attached to the acyl group of a carboxylic acid with other atoms or functional groups, which are known as substituents.

If an alkoxy group (R–O) or phenoxy group (Ar–O) are bonded to the acyl group, the derivative is called an ester.

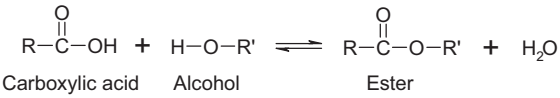


Esters are named by adding the suffix "-oate" to the parent name of the corresponding carboxylic acid and adding a prefix appropriate to the alkoxy or phenoxy group. For example, the acyl group from butanoic acid combined with the alkoxy group derived from the methyl group yields methyl butanoate, a chemical that gives apples their aroma.



Esters are polar molecules; however, because there is no intermolecular hydrogen bonding between the molecules, the boiling point of esters is lower than those of alcohols and carboxylic acids of comparable molecular weight. The oxygen atoms in esters can form hydrogen bonds to the hydrogen in water; thus, esters are slightly soluble in water. They are less soluble than carboxylic acids, though, because they have no hydrogen to form a hydrogen bond to the oxygen in water. Esters have pleasant fruity smells that are responsible for the aroma of many fruits.

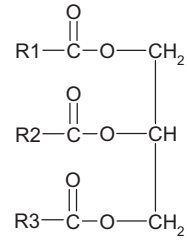
Esters are synthesized from carboxylic acids by condensation reactions with alcohols in the presence of an acid catalyst. In these condensation reactions, known as esterification, the carboxylic acid supplies the hydroxyl group, while the alcohol supplies the hydrogen to form water. According to Le Chaterlier's principle, distilling water out of the reaction mixture can increase the yield of ester. Likewise, reacting in the presence of excess alcohol can increase the ester yield.



Hydrolysis of esters, catalyzed by a strong acid, is the reverse reaction of esterification, yielding a carboxylic acid and an alcohol as products. However, if hydrolysis occurs in the presence of a strong base, the conjugate base of the carboxylic acid, known as a carboxylate ion, forms instead of the acid. This process is called saponification, from the Latin word for soap, because soaps are the salts of long-chain carboxylic acids (metal carboxylates).

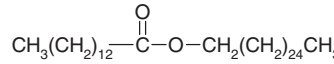
Triglycerides, also known as fats and oils, are a special class of esters that consist of three long-chain fatty (carboxylic) acids attached to a backbone of glycerol (1,2,3-propanetriol). The acid fractions of triglycerides can vary in chain length and degree of saturation. Fats, which are solid or semi-solid at room temperature, have a high percentage of saturated acids, whereas oils, which are liquid at room temperature,

have a high percentage of unsaturated acids. Plant-derived triglycerides are typically oils containing unsaturated fatty acids, including oleic, linoleic, and linolenic acids.



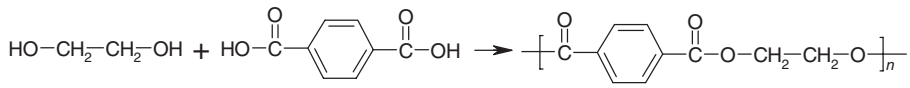
Triglyceride

Waxes are another class of esters consisting of fatty acids and long-chain alcohols containing an even number of carbon atoms. Waxes are low-melting solids that coat the surface of plant leaves and fruits, and also the hair and feathers of some animals. Waxes are usually a complex mixture of several esters. For example, hydrolysis of bees wax yields several fatty acids and a mixture of alcohols containing 24–36 carbon atoms.



An ester found in beeswax

Polyesters are produced by the reaction of carboxylic acids and alcohols that contain two or more functional groups. These acid-catalyzed condensation reactions yield long chains of repeating ester groups that represent an important class of synthetic polymers. One of the most important polyesters, poly(ethylene terephthalate) or PET, is produced by the reaction of 1,2-ethanediol (ethylene glycol) with benzene-1,4-dicarboxylic acid (terephthalic acid), which is spun into fibers and marketed as Dacron.



1,2-Ethanediol Benzene-1,4-Dicarboxylic acid Poly(ethylene terephthalate)

3.4.9 Other Functional Groups

Other carboxylic acid derivatives include amides, in which a substituent is linked to the acyl group by a nitrogen atom; thioesters, in which the substituent is linked to the acyl group by a sulfur atom; acyl chlorides, in which the substituent linked to the acyl group is a chlorine atom; and acid anhydrides, in which two acyl groups are linked by an oxygen atom.

Organic compounds with one or more carbon–nitrogen single bonds are amines. Compound with carbon–nitrogen double and triple bonds are imines and nitriles,

respectively. Sulfur forms single bonds to carbon in two classes of compounds. Thiols (also called mercaptans) and thioethers (also called sulfides) structurally resemble alcohols and ethers, which contain oxygen, another element in the same group of the periodic table as sulfur.

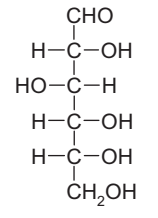
3.5 Chemistry of Lignocellulosic Plant Materials

3.5.1 Carbohydrates

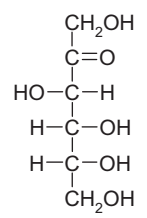
Carbohydrates are polyhydroxy aldehydes, polyhydroxy ketones, or compounds that can be hydrolyzed from them. Carbohydrates, which are designated with the suffix "-ose," range in size from molecules containing three carbon atoms to gigantic molecules containing thousands of carbon atoms. The smallest carbohydrates, those that cannot be hydrolyzed to smaller carbohydrate units, are called monosaccharides.

Carbohydrates consisting of a few monosaccharides are called oligosaccharides. Those consisting of two monosaccharides, which may be the same or different compound, are called disaccharides. Examples include lactose and maltose. Polysaccharides contain thousands of covalently linked monosaccharides. Starch and cellulose are examples of homopolysacccharides, which are polysaccharides containing only one kind of monosaccharide. Polysaccharides that contain different kinds of monosaccharides are called heteropolysaccharides. Acetal or ketal bonds link the monosaccharides in oligo- and polysaccharides; these can be hydrolyzed to yield the component monosaccharides.

Monosaccharides are classified according to their most highly oxidized functional group, either an aldehyde group or a ketone group. Aldoses contain a single aldehyde group, while ketoses contain a single ketone group. Monosaccharides are designated with the prefix aldo- or keto-, as appropriate, and the prefix tri-, tetra-, pent-, and hex- to indicate the number of carbon atoms. For example, D-glucose and D-fructose are 6-carbon monosaccharides isomers with the molecular formula of $C_6H_{12}O_6$. However, D-glucose contains an aldehyde group as the first carbon atom in the chain, making it an aldohexose, while D-fructose contains a ketone group as the second carbon atom in the chain, making it a ketohexose.



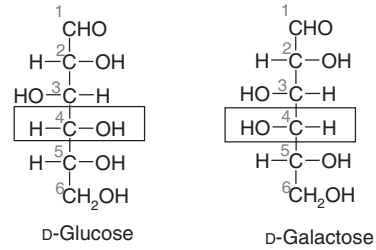
D-Glucose
(an aldohexose)



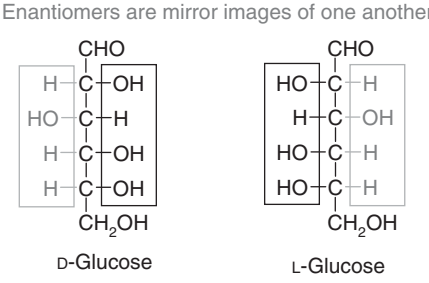
D-Fructose
(a ketohexose)

D-Glucose is the carbohydrate around which metabolism is based, and D-fructose is the sugar commonly found in fruits and honey. Because of the differences in functional groups, D-glucose and D-fructose qualify as functional isomers of one another.

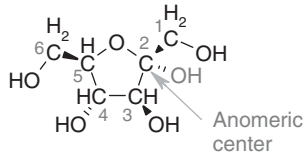
The monosaccharides also include stereoisomers—those that have the same sequence of bonded atoms but differ only in the spatial location of atoms or functional groups around the carbon chain. Of particular interest are epimers, isomers that differ in spatial arrangement only about a single carbon atom in the chain. D-Galactose, like D-glucose, is an aldohexose with molecular formula $C_6H_{12}O_6$. They differ only in the position of the hydroxyl group attached to the fourth carbon atom (where carbon atoms are numbered starting at the end of the chain closest to the carbonyl carbon atom); thus, they are known as C-4 epimers. Although physical and chemical properties of epimers are essentially the same, biological activity can be quite different.



A special instance of positional isomers among monosaccharides is based on chirality. A molecule is chiral if it is not superimposable on its mirror image; otherwise, it is achiral. Chiral molecules have the same chemical formulas but can be arranged in two different ways corresponding to the mirror images of one another; these are known as enantiomers. In carbohydrate chemistry, enantiomers are designated by either the suffix D- or L-, the former being used for enantiomers that correspond to the chirality of the naturally occurring enantiomer of glyceraldehyde, a three-carbon monosaccharide. Because monosaccharides in nature are derived from the building block D-glyceraldehyde, nearly all naturally derived monosaccharides are of the D series. Thus, the D- or L-suffix is commonly discarded when discussing monosaccharides, with the D series assumed.

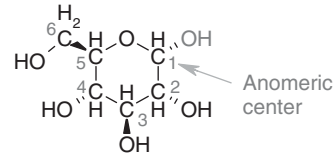


Recall that the carbonyl group of aldehydes and ketones can react reversibly with the hydroxyl group of alcohols to form hemiacetals and hemiketals, respectively. Furthermore, if the carbonyl group and the hydroxyl groups occur in the same compound, they can react to form cyclic structures known as cyclic hemiacetals and cyclic hemiketals. Monosaccharides contain both carbonyl groups and hydroxyl groups and, thus, readily form cyclic structures. Indeed, hemiacetal forms of aldohexoses and aldopentoses predominate over open chain five-carbon and six-carbon aldoses, while hemiketal forms of ketohexoses and ketopentoses predominate over open chain five-carbon and six-carbon ketoses. Cyclic hemiacetals and cyclic hemiketals of carbohydrates that form five-membered rings are called furanoses; those that form six-membered rings are called pyranoses. The carbon atoms are numbered starting with the carbon atom nearest to the carbon atom at the anomeric center.



Perspective structural formula of a furanose

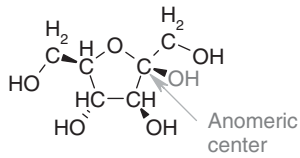
(α-D-Fructofuranose)



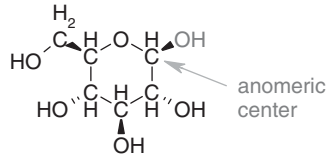
Perspective structural formula of a pyranose

(α-D-Glucopyranose)

The carbon atom around which the hemiacetal or hemiketal structure forms is called the anomeric carbon atom or anomeric center. Note that it is the only carbon atom in the monomer attached to two oxygen atoms. Also note that the hydroxyl groups attached to the anomeric centers of the furanose and pyranose molecules illustrated above are directed below the plane of the cyclic structure (as indicated by the dashed wedge used to represent the C–OH bond). This isomeric form is designated by the prefix α-; thus, the hemiketal form of D-fructose with a downward projecting hydroxyl group attached to the anomeric center is called α-D-fructofuranose, while the hemiacetal form of D-glucose with a downward projecting hydroxyl group attached to the anomeric center is called α-D-glucopyranose. The epimers of these monosaccharides have the hydroxyl group associated with the anomeric center projecting upward and are designated with a prefix β-.

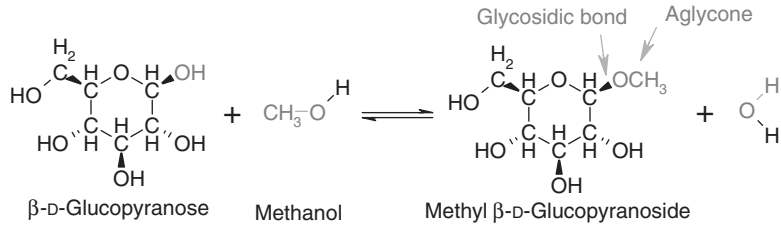


β-D-Fructofuranose

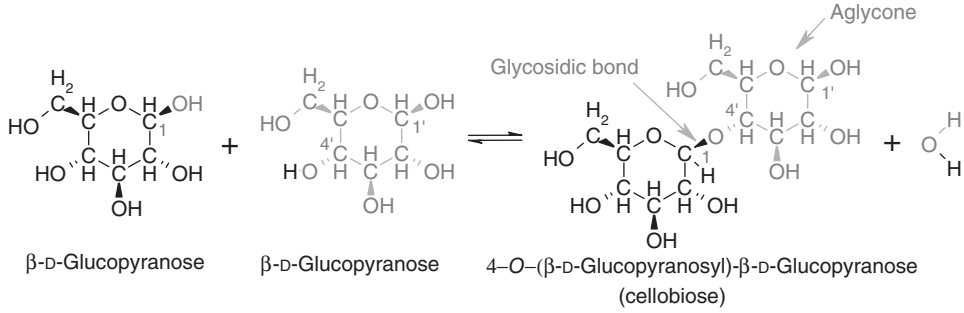


β-D-Glucopyranose

Recall that the hemiacetal and hemiketals can react with alcohols to form acetals and ketals. The acetals and ketals produced from the cyclic hemiacetal and hemiketal forms of monosaccharides are called glycosides, and the C–O bond thus formed is called the glycosidic bond. The group bonded to the anomeric carbon atom of a glycoside is an aglycone.



These glycosidic bonds are the basis for constructing oligosaccharides and polysaccharides from monosaccharides because they allow linkage between the anomeric center of one monosaccharide with a hydroxyl oxygen atom of a second monosaccharide. Consider the bonding of two D-glucose monosaccharides in their cyclic forms of β-D-glucopyranose: a glycosidic bond is formed between the anomeric center of the first monosaccharide (designated the C-1 carbon atom) and one of the hydroxyl carbon atoms of the second monosaccharide. If the fourth carbon atom of the second monosaccharide is involved (called the C-4′ carbon atom), the resulting disaccharide is called cellobiose, the structural unit of cellulose. The IUPAC name is 4-*O*-(β-D-glucopyranosyl)-β-D-glucopyranose. The -syl suffix on the first monosaccharide parent name indicates that this unit is linked to the second unit by a glycosidic bond. The prefix 4-*O* refers to the position of the oxygen atom of the aglycone unit.

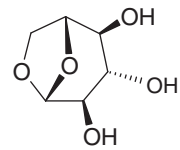


Note that the reverse of this disaccharide-building reaction is hydrolysis of an oligosaccharide to release monosaccharides.

Other common disaccharides are maltose, a combination of α-D-glucopyranose and β-D-glucopyranose by a α-1,4′-glycosidic bond; lactose, a combination of β-D-galactopyranose and β-D-glucopyranose by a β-1,4′-glycosidic bond; and

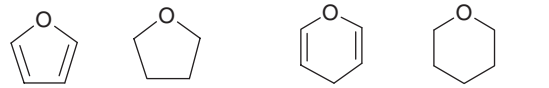
sucrose, a combination of α-D-glucopyranose and β-D-fructofuranose linked by their anomeric centers by both a α-glycosidic bond on the glucose and a β-glycosidic bond on the fructose.

Dehydrated sugars play a prominent role in thermochemical conversion of polysaccharides. Whereas depolymerization of polysaccharides in an aqueous environment produces monosaccharides through the action of hydrolysis, the scarcity of water during thermal depolymerization of polysaccharides in a gaseous environment results in monosaccharides that are missing the water molecule inserted during aqueous-phase hydrolysis. These singly dehydrated sugars are called anhydrosugars. The dehydrated analogs of sugars with six-member rings are called anhydropyranoses, while the dehydrated analogs of sugars with five-member rings are called anhydrofuranoses. For example, cellulose, a polymer of glucose monomers ($C_6H_{12}O_6$), can thermally depolymerize to 1,6-anhydro-β-D-glucopyranose ($C_6H_{10}O_5$), commonly known as levoglucosan.



1,6-Anhydro-β-D-Glucopyranose (levoglucosan)

Multiple dehydration products of monosaccharides can also occur including five-member aromatic ethers known as furans; five-member saturated ring ethers known as tetrahydrofurans; six-member unsaturated ring ethers known as pyrans; and six-member saturated ring ethers known as tetrahydropyrans. These ring ethers typically include multiple functional group substitutions.



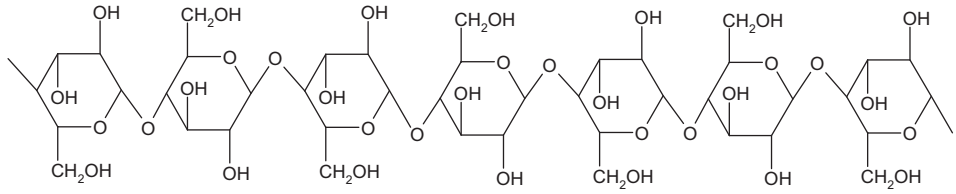
Furan Tetrahydrofuran Pyran Tetrahydropyran

Among the most important polysaccharides in nature are starch, cellulose, and hemicellulose. Starch is a polymer of α-1,4-linked glucose molecules consisting of the disaccharide maltose as the basic structural unit. Starch, an important energy source in nature, accumulates as granules in the cells of many kinds of plants. Starch occurs as both linear molecules, known as amylose, and branched molecules, known as amylopectin. Different plants accumulate various proportions of amylose and amylopectin. Cellulose and hemicellulose are discussed in the next section.

3.5.2 Lignocellulose

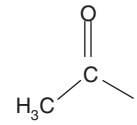
Lignocellulose is the term used to describe the three-dimensional polymeric composites formed by plants as structural material. It consists of variable amounts of cellulose, hemicellulose, and lignin. Hardwoods (from deciduous trees), softwoods (from coniferous trees), and herbaceous material (from grasses and agricultural crops) have distinct compositions from one another, as detailed in Chapter 4.

Cellulose, a homopolysaccharide of glucose, is an important constituent of most plants.



The basic building block of this linear polymer is cellobiose, a compound of two glucose molecules. The number of glucose units in a cellulose chain is known as the degree of polymerization (DP). The average DP for native cellulose is on the order of 10 000, although chemical pulping reduces this to the range of 500–2000. Cellulose molecules are randomly oriented with a tendency to form intra- and intermolecular hydrogen bonds. The strong tendency for intra- and intermolecular hydrogen bonding in cellulose results in molecular aggregation to form microfibrils. High packing densities result in highly ordered microfibrils known as crystalline cellulose. Low packing densities result in less ordered microfibrils known as amorphous cellulose. Crystalline cellulose is relatively inert to chemical treatment and insoluble in most solvents.

Hemicellulose is a large number of heteropolysaccharides built from hexoses (D-glucose, D-mannose, and D-galactose), pentoses (D-xylose, L-arabinose, and D-arabinose), and deoxyhexoses (L-rhamnose or 6-deoxy-L-mannose and rare L-fucose or 6-deoxy-L-galactose). Xylan is a general term to describe the predominant hemicellulose in most plants, which is built of a backbone of β-(1→4)-D-xylopyranose with a variety of side chains. The composition and linkages of the side chains vary among types of plants. Because the side chains of grasses and annuals are mainly arabinofuranoses and acetyl groups, these xylans are referred to as arabinoxylans. The ester-linked acetyl groups are attached to C2 or C3 hydroxyl groups.



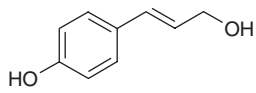
Acetyl functionality

Hardwood xylans are termed glucuronoxylans because they are highly substituted with acetyl and 4-*O*-methyl glucuronic acid (a carboxylic acid with a ring structure similar to glucose). 4-*O*-methylglucuronic acid is linked to the xylan backbone by α-(1→2) glycosidic bonds, while the acetic acid is esterified at the two- and/or three-carbon hydroxyl groups. The molar ratio of xylose/glucuronic acid/acetyl residues is about 10:1:7.

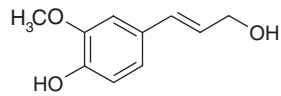
In contrast, softwood hemicellulose is dominated by galactose and mannose units (known as galactoglucomannan) (15–20% dry biomass weight), with xylans comprising only 7–10% of the biomass dry weight. The galactoglucomannans are divided into two subtypes of low and high galactose content with galactose/glucose/mannose ratios of 0.1:1:4 and 1:1:3, respectively. Softwood xylans are not acetylated but are more highly substituted with 4-*O*-methyl glucuronic acid than are hardwood xylans.

The monosaccharides released upon hydrolysis of hemicellulose include a large fraction of pentoses as opposed to hexose from cellulose. The chemical and thermal stability of hemicelluloses is lower than that of cellulose, presumably due to their lack of crystallinity and lower DP, which is only 100–200.

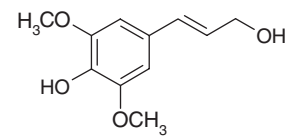
Lignin, illustrated in Figure 3.1, is a phenylpropane-based polymer and the largest non-carbohydrate fraction of lignocellulose. It is constructed of three monomers—paracoumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, each of which has an aromatic ring with different substituents.



Paracoumaryl alcohol



Coniferyl alcohol



Sinapyl alcohol

The functional groups associated with lignin, including phenolic and alcoholic hydroxyl groups, and aldehyde (CHO–) and methoxy (CH_3O–) groups result in highly reactive molecules. The number of various functional groups per 100 phenylpropane (C_6H_3) units is given in Table 3.4 for hardwoods and softwoods. Lignin can be depolymerized by heat or laccase or peroxidase enzymes although not necessarily back to its original building block monomers. Lignin and hemicellulose form a sheath that surrounds the cellulosic portion of the biomass. Lignin protects lignocellulose against pests.

Natural lignins are roughly classified according to plant source: softwood, hardwood, and grasses. Attempts to chemically liberate lignin from lignocellulose almost always produce a modified product distinct from the natural form with different physical and chemical properties. Thus, it is common to distinguish lignin by the process that liberated it: kraft or sulfate lignin from kraft pulping; alkali or soda lignin from soda processing; lignosulfonates from sulfite pulping; organosolv lignin from treating wood with alcohol solvents; acid hydrolysis and enzymatic hydrolysis lignins from these respective processes to "saccharify" lignocellulose;

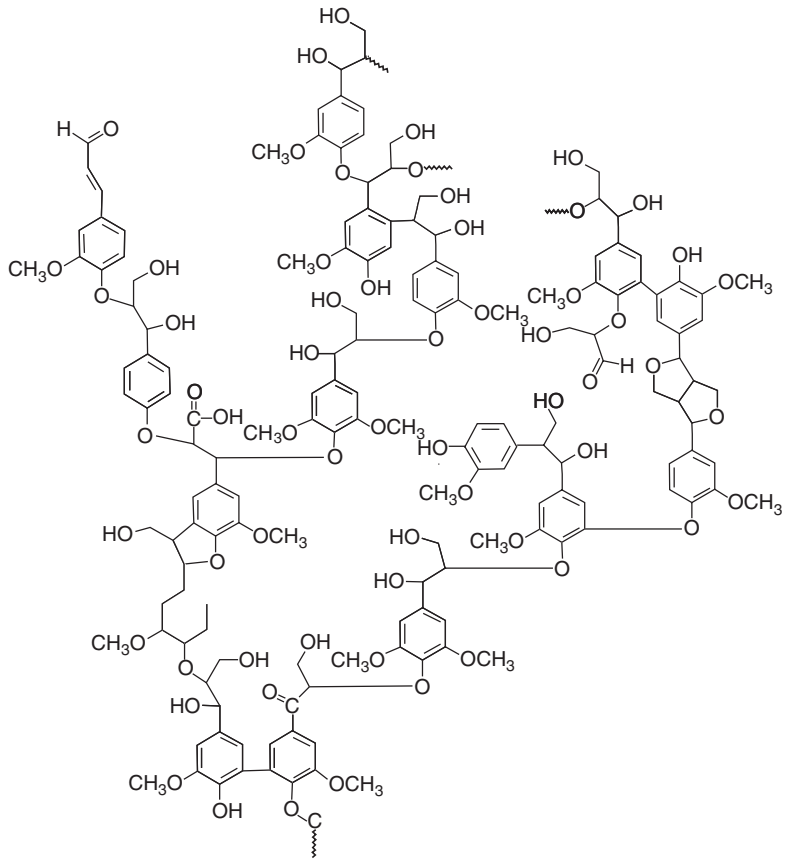


Fig. 3.1 Polymeric structure of softwood lignin. Adapted from Adler, E. (1977) Lignin chemistry—past, present and future. *Wood Science Technology*, 11, 169–218.

and pyrolytic lignin from the pyrolysis of lignocellulose. The lignin is condensed to different degrees by these processes. Very fine mechanical milling of wood can liberate "milled wood" lignin, which is thought to be very close to natural lignin in composition and chemistry.

Plant materials also contain thousands of other chemical compounds known as "extractives." These include resins, fats and fatty acids, phenolics, phytosterols,

Table 3.4 Number of functional groups in natural lignin (per 100 C_6H_3 units)

Functional Group	Softwood Lignin	Hardwood Lignin
Phenolic hydroxyl (Ar–OH)	20–30	10–20
Aliphatic hydroxyl (R–OH)	115–120	110–115
Methoxyl (CH_3O–)	90–95	140–160
Aldehyde (CHO–)	20	15

and other compounds, the content of which is extremely dependent on the plant species. These are often classified as either hydrophilic or lipophilic depending on whether they are soluble in water or organic solvents, respectively. Resin is often used to describe the lipophilic extractives with the exception of phenolic substances. Extractives impart color, odor, and taste to wood. Although some extractives (lipids) are an energy source for the plant, the functions of most appear to protect the plant against microbiological damage or insect attacks. They are a valuable byproduct of many manufacturing processes, especially in the pulp and paper industry. For example, southern pines, favored in pulp making, have particularly high content of extractives, which are recovered as crude turpentine and raw tall oil.

The cell walls of both woody and herbaceous biomass consist of lignocellulose. These cells can be classified into two broad categories: prosenchyma cells, which are long, thin cells, with flattened or tapered closed ends, and parenchyma cells, which are short, rectangular cells. Prosenchyma cells are on the order of 1–6 mm in length with widths of 20–50 μm. Parenchyma cells are shorter than 0.2 mm with widths of 2–50 μm.

Softwoods consist primarily of prosenchyma cells, about 90% of the total, referred to as tracheids, which both transport fluids through the plant and support the plant. These are long, strong fibers ideal for pulp and paper applications. Parenchyma cells provide storage of nutrients in softwoods.

Hardwoods consist of a much smaller fraction of prosenchyma cells, about 55% of the total, along with a significant fraction of parenchyma cells, about 20%, and cells intermediate in size to prosenchyma and parenchyma cells known as vessel cells. In hardwoods, prosenchyma cells provide structural support, parenchyma cells provide both transport of fluids and nutrient storage, and vessel cells serve primarily for transport. Herbaceous plant material more closely resembles hardwoods than softwoods.

Further Reading

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Plant Chemistry

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CHAPTER

4

The Biorenewable Resource Base

4.1 Defining the Resource

Biorenewable resources, sometimes referred to as *biomass*, are organic materials of recent biological origin. This definition is deliberately broad with the intent of only excluding fossil fuel resources from the wide variety of organic materials that arise from the biotic environment. Biorenewable resources are generally classified as either *wastes* or *dedicated energy crops*.

A waste is a material that has been traditionally discarded because it has no apparent value or represents a nuisance or even a pollutant to the local environment. Clearly, if so-called wastes from one process were utilized as feedstock in another process, a more appropriate name would be coproducts. For example, oat-processing plants often generate enormous quantities of agricultural residues in the form of hulls that are currently viewed as wastes. If economically converted into process heat, electricity, liquid fuels, or chemicals, they would be considered a coproduct rather than a waste stream. This holistic approach to manufacturing, in which all the outputs from one process become the inputs to other processes, is known as *industrial ecology*. However, the word "wastes" remains a convenient moniker for "low-value coproducts" and will be used in this book.

Dedicated energy crops are plants grown specifically for production of biobased products; that is, for purposes or than food or feed. The term was originally coined to describe woody or herbaceous plants grown for their high yields of lignocellulosic material, which can be burned in a power plant to produce electricity or hydrolyzed to release fermentable sugars suitable for the production of transportation fuels. However, not all dedicated energy crops are grown for fuels and energy (they might be used for production of commodity chemicals or natural fibers), and not all fuels and energy products are derived from lignocellulosic crops (indeed, fuel ethanol is currently produced from corn starch in the United States and sugarcane in Brazil). Thus, the term "dedicated energy crop" is something of a misnomer, but it has wide usage and is understood to mean crops grown specifically as a source of carbon and energy for the manufacture of biobased products.

Biorenewable Resources: Engineering New Products from Agriculture, Second Edition. Robert C. Brown and Tristan R. Brown.
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4.2 Waste Materials

Categories of waste materials that qualify as biorenewable resources include agricultural residues, yard waste, municipal solid waste (MSW), food processing waste, manure, and even invasive flora or blighted stands of plants that are harvested as part of an effort to control the contagion. Agricultural residues are simply that part of a crop discarded after harvest such as corn stover (see Figure 4.1), rice hulls, wheat straw, bagasse (fibrous material remaining after the milling of sugarcane), grapevine prunings, and almond shells, to name a few. Yard waste is an urban biomass crop: grass clippings, leaves, and tree trimmings. Invasive flora are plants or microorganisms that spread into non-native habitat. Blighted stands refer to widespread infection of a particular species of plant in an ecosystem.

Municipal solid waste is whatever is thrown out in the garbage, not all of which is suitable as biomass feedstock. In some communities, yard waste may constitute up to 18% of MSW, although a growing number of communities have ordinances against disposal of yard waste with garbage in an effort to conserve landfill space. In communities where yard waste is excluded from MSW, the important components are paper (50%), plastics and other fossil fuel–derived materials (20%), and food wastes (10%). Nonflammable materials (glass and metal) represent 20% of MSW.

Food processing waste is the effluent from a wide variety of industries ranging from breakfast cereal manufacturers to alcohol breweries. These wastes may be dry solids or watery liquids. Sewage represents a source of chemical energy and is often converted into electric power at municipal wastewater treatment plants.

The recent concentration of animals into giant livestock facilities has led to calls to treat animal wastes in a manner similar to that for human wastes. Consequently, many strategies for manure management integrate waste treatment with heat and power generation.

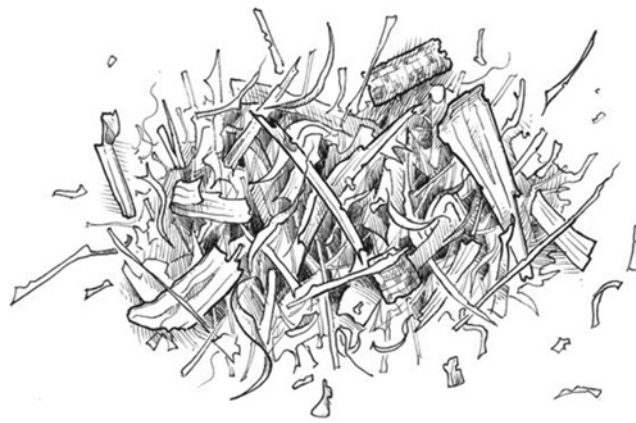

Fig. 4.1 Corn stover.

Invasive flora are plants that have been accidently or sometimes deliberately introduced into a non-native ecosystem where they often thrive because of the absence of natural controls such as herbivores or insects that prey on them. More commonly known as weeds, these plants can quickly dominate an ecosystem causing great damage. Examples are mesquite trees in many semiarid regions of the world and brown kelp along coastal California. Many were deliberately introduced into non-native regions in ill-considered attempts to cultivate them for various commercial purposes. Although invasive species might seem an unlikely supply of biomass, in fact, when they dominate a landscape, harvesting them becomes economically feasible while also helping control their spread. Both mesquite and kelp harvesting have been proposed for just such purposes.

Similarly, blighted stands of plants could be harvested as a supply of biomass as part of an effort to control the contagion. However, this requires local processing of the infected material in a manner that destroys the infectious agent to keep it from spreading, as often occurred in the past when infected trees were harvested and transported to distant sawmills. Thermal processing, as described in Chapter 8, would be particularly effective in destroying infectious agents, whether insects, bacteria, or viruses.

Waste materials share few common traits other than the difficulty of characterizing them because of their variable and complex composition. MSW is the leavings of thousands of households and industries that yield a feedstock that may be easy to process one day and difficult the next. Yard wastes show seasonal variations in quantity and composition: the spring brings high-moisture grass clippings that are replaced by dry leaves in the autumn. Waste streams from food processing plants, on the other hand, may be relatively invariant in composition but contain a wide assortment of complex organic compounds that are not amenable to a single conversion process. Thus, waste biomass presents special problems to engineers who are tasked with converting this sometimes unpredictable feedstock into reliable power or high-quality fuels and chemicals.

The major virtue of waste materials is their low cost. By definition, waste materials have little apparent economic value and often can be acquired for little more than the cost of transporting the material from its point of origin to a processing plant. Increasing costs for solid waste disposal and sewer discharges and restrictions on landfilling certain kinds of wastes allow some wastes to be acquired at negative cost; that is, a biorenewable resource processing plant is paid by a company seeking to dispose of a waste stream. For this reason, many of the most economically attractive opportunities in biorenewable resources involve waste feedstocks. For example, the seed corn industry, which sells seed grown specifically for planting new crops, has an annual waste disposal problem. Seed for which germination cannot be guaranteed after a certain period of storage is taken off the market. This seed cannot be sold for animal feed or even landfilled because the seed is treated with fungicide. Seed corn companies often pay brokers

to accept this obsolete seed who, in turn, sell it as an inexpensive fuel for boilers and cement kilns.

As demand for these newfound feedstocks increases, those that generate them come to view themselves as suppliers and may demand payment for their waste stream: a negative feedstock cost becomes a positive one. Such a situation developed in the California biomass power industry during the 1980s. Concerns about air pollution in California led to restrictions on open-field burning of agricultural residues, a practice designed to control infestations of pests. With no means for getting rid of these residues, an enormous reserve of biomass feedstocks was materialized. These feedstocks were so inexpensive that independent power producers recognized that even small, inefficient power plants using these materials as fuel would be profitable. A number of plants were constructed and operated on agricultural residues. Eventually, the plant operators bid up the cost of this once valueless waste material. In the end, many of these plants were closed in part because of the escalating cost of biomass feedstock.

4.3 Dedicated Energy Crops

Dedicated energy crops are terrestrial plants and aquatic species grown specifically for applications other than food or feed. It is important to note that firewood obtained from cutting down an old-growth forest does not constitute a dedicated energy crop. A dedicated energy crop is grown and harvested periodically. Harvesting may occur on an annual basis, as with sugar beets or switchgrass, or on a 5–7-year cycle, as with certain strains of fast-growing trees such as hybrid poplar or willow, or even continuously, as with microalgae. The cycle of growth, harvesting, and regrowth over a relatively short time period assures that the resource is used in a sustainable fashion; that is, the resource will be available for future generations.

Dedicated energy crops can fulfill one or more market niches. In some instances, the whole plant is used as feedstock for production of electricity and/or liquid fuels. Such is the case when trees are grown and harvested specifically as boiler fuel for steam power plants. Another possibility is that a variety of coproducts are coaxed from a single crop. For example, alfalfa has been evaluated for its potential to yield both energy and feed from a single crop. The high-protein leaves would be removed after harvesting and processed into animal feed, while the fibrous stems would be used as fuel in a gasification power plant. The least desirable and most wasteful scenario for dedicated energy crops is extraction of the highest-value portion of the crop for conversion into biobased product and discarding the rest of the plant as waste.

Dedicated energy crops contain significant quantities of one or more of four important energy-rich components: oils, sugars, starches, and lignocellulose (fiber). Crops rich in the first three have historically been grown for food and feed: oils from

soybeans, nuts, and grains; sugars from sugar beets, sorghum, and sugarcane; and starches from corn and cereal crops. Oil, sugars, and starches are easily metabolized. On the other hand, lignocellulose is indigestible by humans although certain domesticated animals with specialized digestive tracts are able to break down the polymeric structure of lignocellulose and use it as an energy source. From this discussion, it might appear that the best strategy for developing biomass resources is to grow crops rich in oils, sugars, and starches. However, most terrestrial plants, even those known as "oil crops" or "starch crops," are mostly lignocellulose, the structural (fibrous) material of plants: hulls, shells, stems, leaves, and roots. If oils, sugars, and starches are harvested and the lignocellulose is left behind as agricultural residue rather than used as fuel or feedstock, a large portion of the biomass crop remains in the field.

Not only should lignocellulose be valued, there is good reason to maximize its production at the expense of lipids and simple carbohydrates if energy production or commodity chemicals are the primary purpose for growing the crop. Research has shown that energy yields (kilojoules per hectare per year) are usually greatest for plants that are mostly "roots and stems"; in other words, plant resources are directed toward the manufacture of lignocellulose rather than oils, sugars, and starches. As a result, there has been a bias toward the development of dedicated energy crops that focus on lignocellulosic biomass, at least for vascular flora (i.e., plants with an internal system for transport of water and nutrients).

Exceptions to this rule-of-thumb are many non-vascular (eukaryote) floras from the phyla *Chlorophyta* (green algae), *Rhodophyta* (red algae), *Phaeophyta* (brown algae, the kelps), and *Bryophyta* (mosses and liverworts) and the prokaryote *Cyanobacteria* (blue-green algae). The term flora is used to avoid confusion in the classification of certain kinds of photosynthetic organisms. At one time, nonvascular flora were considered to be simple plants (kingdom Plantae) but are now classified in the kingdom Protist. Further complicating the nomenclature, blue-green algae were found to be neither plants nor protists but members of the separate kingdom Bacteria.

These non-vascular flora either live as low-growing plants in wet terrestrial environments or as aquatic species. Because non-vascular flora do not require the structural support of vascular terrestrial plants, they do not incorporate lignocellulose into their cell walls. Although they may contain amorphous polysaccharides like starch, lignin is absent. In many unicellular photosynthetic organisms, lipids and protein can be the major constituents of the biomass.

Dedicated energy crops are conveniently divided into three categories: herbaceous energy crops (HEC) and short rotation woody crops (SRWC), both of which represent lignocellulosic-rich vascular plants, and oleaginous (lipid-rich) crops, which includes both oil seed (vascular) plants and non-vascular microalgae and cyanobacteria. Selected feedstocks are described in the following sections and Appendix A.

4.3.1 Herbaceous Energy Crops

Herbaceous crops are plants that have little or no woody tissue. The aboveground growth of these plants usually lives for only a single growing season. However, herbaceous crops include both annuals and perennials. Annuals die at the end of a growing season and must be replanted in the spring. Perennials die each year in temperate climates but reestablish themselves each spring from rootstock. Both annual and perennial HEC are harvested on at least an annual basis, if not more frequently, with yields averaging 5.5–11 Mg/ha/year, with maximum yields between 20 and 40 Mg/ha/year in temperate regions. As with trees, yields can be much higher in tropical and subtropical regions.

Among the many species of herbaceous plants that are potentially suitable as dedicated energy crops, recent development work has focused on grasses because of their high yields of lignocellulose. Grasses are conveniently classified as either thick stemmed or thin stemmed. Thick-stemmed grasses, which include annual and perennial varieties, are indigenous to the tropics. The most familiar examples are sugarcane and energy cane (*Sacharum* spp.), miscanthus (*Miscanthus giganteus*, illustrated in Figure 4.2), and Napier grass (*Pennisetum purpureum*) among the perennials and corn (*Zea mays*) and forage sorghum (sorghum, Sudan grass, and sorghum × Sudan grass, now all classified as *Sorghum bicolor*) among the annuals.

FIG. 4.2 Miscanthus (*Miscanthus giganteus*).

Harvesting of thick-stemmed perennials such as sugarcane is a labor-intensive activity even with mechanized harvesting equipment. Cost-effective harvesting of thick-stemmed perennials as HEC would probably be by forage harvesters followed by storage as silage. The same is true of many of the thick-stemmed annuals although dry corn stalks can be baled readily.

Thin-stemmed grasses include many perennial and annual species. These are conveniently classified as either cool-season grasses, which grow more vigorously in the spring and fall, or warm-season grasses, which grow most actively during the summer. Familiar perennial cool-season grasses include reed canary grass (*Phalaris arundinacea*), Timothy-grass (*Phleum pratense*), and tall fescue (*Festuca arundinacea*). Examples of warm-season grasses are switchgrass (*Panicum virgatum*, illustrated in Figure 4.3), big bluestem (*Andropogon gerardii*), and eastern gamagrass (*Tripsacum dactyloides*).

The thin-stemmed perennials are particularly attractive as HEC because they can be harvested with conventional hay equipment. They are less susceptible to

FIG. 4.3 Switchgrass (*Panicum virgatum*).

lodging (falling over on one another as the plants become tall) than the thick-stemmed grasses. This is important because it allows the plants to be harvested at the end of the growing season when valuable nutrients have translocated to roots. Perennials, as a rule, are more drought resistant than annuals, require less weed control, and are less likely to erode soils. Warm-season, thin-stemmed grasses are the leading candidates for HEC. They are more drought resistant than cool-season grasses and are efficient users of nutrients.

Herbaceous crops more closely resemble hardwoods in their chemical properties than they do softwoods. Their low lignin content makes them relatively easy to delignify, which improves accessibility of the carbohydrate in the lignocellulose, especially for biochemical processing. The hemicellulose contains mostly xylan, which is highly susceptible to acid hydrolysis, compared to the cellulose. As a result, agricultural residues are susceptible to microbial degradation, destroying their processing potential in a matter of days if exposed to the elements. Herbaceous crops have relatively high silica content compared to woody crops, which can present problems during processing.

4.3.2 Short Rotation Woody Crops

Short rotation woody crop is used to describe woody biomass that is fast growing and suitable for use in dedicated feedstock supply systems. Desirable SRWC candidates display rapid juvenile growth, wide site adaptability, and pest and disease resistance. Woody crops grown on a sustainable basis are harvested on a rotation of 3–10 years.

Woody crops include hardwoods and softwoods. Hardwoods are trees classified as angiosperms, which are also known as flowering plants. Examples include willow, oak, and poplar. Hardwoods can resprout from stumps, a process known as coppicing, which reduces their production costs compared to softwoods. Advantages of hardwoods in processing include: high density for many species; relative ease of delignification and accessibility of wood carbohydrates; the presence of hemicellulose high in xylan, which can be removed relatively easily; low content of ash, particularly silica, compared to softwoods and herbaceous crops; and high acetyl content compared to most softwoods and herbaceous crops, which is an advantage in the recovery of acetic acid. Hardwood lignin is less condensed (i.e., lower degree of polymerization) than softwood and contains a greater methoxyl content, which accounts for its preference at one time for the destructive distillation of wood to produce methanol. Hardwood lignin becomes plastic at lower temperatures than for softwood lignin.

Softwoods are trees classified as gymnosperms, which encompass most trees known as evergreens. Examples include pine, spruce, and cedar. Softwoods are generally fast growing, but their carbohydrate is not as accessible for chemical processing as the carbohydrates in hardwood. Since softwoods have considerable

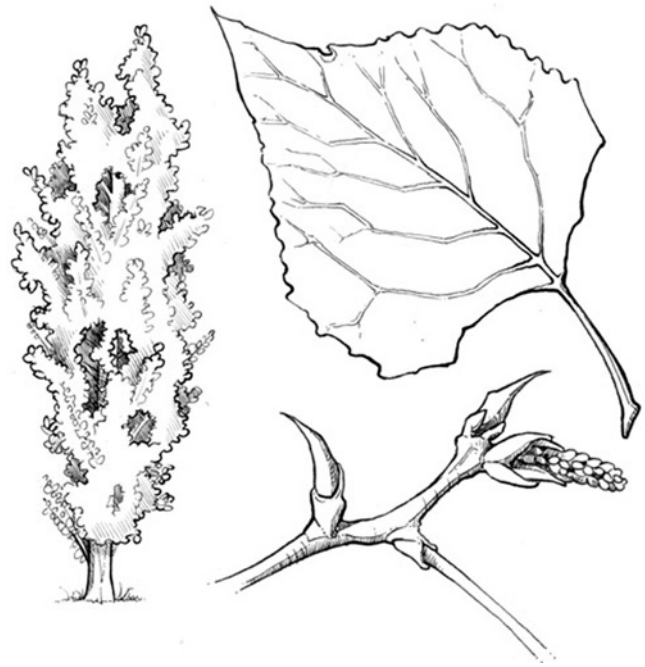

FIG. 4.4 Hybrid poplar (*Populus nigra*).

value as construction lumber and pulpwood, it is more readily available as waste material in the form of logging and manufacturing residues than are hardwoods. Logging residues, consisting of a high proportion of branches and tops, contain considerable high-density compression wood, which is not easily delignified. Logging residues are more suitable as boiler fuel or other thermochemical treatments than as feedstock for chemical or enzymatic processing.

Development of dedicated feedstock supply systems has focused on several hardwood species, including poplar (*Populus* spp., illustrated in Figure 4.4), willows (*Salix* spp.) silver maple (*Acer saccharinum*), sweetgum (*Liquidambar styraciflua*), sycamore (*Platanus occidentalis*), black locust (*Robinia pseudoacacia*), and eucalyptus. Trees of potential regional importance in the United States include alders (*Alnus* spp.), mesquite (*Prosopis* spp.), and the Chinese tallow (*Sapium sebiferum*).

Hybrid poplar and eucalyptus are most promising for the United States because of high growth rates averaging between 10 and 17 Mg/ha/year, depending upon geographic location, with maximum yields between 15 and 43 Mg/ha/year. In the United States, hybrid poplar has a wider range than eucalyptus, which is limited to southern Florida, California, and Hawaii. Hybrid poplar is also attractive for the ease of propagating it from either stem cuttings or tissue culture.

4.3.3 Oleaginous (Lipid-Rich) Crops

Lipids are a large group of hydrophobic, fat-soluble compounds that include fats, sterols, triglycerides, and waxes. Lipids play several roles in living organisms, including energy storage, cellular structural support as membranes, and intercellular signaling. Storage lipids are particularly important as they are concentrated in discrete lipid bodies, usually as triglycerides although sometimes as fatty waxes, which makes them easier to recover. These storage lipids are distinguished by an absence of charged functionalities and are hence referred to as "neutral lipids." In contrast, "polar lipids" have charged functionalities that allow them to form bilayers that constitute the structure of cell membranes. Polar lipids are difficult to extract and their inorganic contents (phosphorous from phosphates and nitrogen from amides) make them less attractive for fuel synthesis. Vascular plants contain specialized oleaginous plant cells to store neutral lipids in the form of seeds.

Triglycerides, commonly known as vegetable oils, are among the most familiar form of lipids and have been widely used for the production of biodiesel from oil seed crops. Until recently, the potential for significant market penetration of lipid-based biofuels was considered small because of the low productivity of traditional oleaginous crops like soybean and rapeseed, which yield only 450–950 L of biodiesel per hectare. Sunflower, one of the most highly productive vegetable oil crops, only produces 550–1600 L/ha compared to 5800–8700 L of ethanol per hectare of corn crop. Even accounting for the lower energy content of ethanol, the fuel energy obtained per hectare is three to seven times higher for corn ethanol than oilseed biodiesel and even higher for cellulosic biofuels. For this reason, little attention was given to further developing lipid-based fuels until recently.

The drivers for renewed attention to lipid-based fuels are twofold. First, lipids are highly reduced compounds, containing very little oxygen, and in some respects resemble long-chained hydrocarbons found in petroleum-based fuels. As will be subsequently described, lipids can be upgraded in a fashion similar to hydroprocessing of petroleum to yield hydrocarbons that are essentially indistinguishable from gasoline, diesel fuel, and aviation fuel. These so-called "drop-in" biofuels can be directly substituted for petroleum-based fuels without modifying fuel distribution or fuel utilization infrastructure. This is especially important for aviation applications where the hydroscopic (water attracting) properties of ethanol make it unsuitable as aviation fuel. The second driver for renewed interest in lipid-based fuels is the prospect for growing high-yielding lipid feedstocks, sometimes in environments not otherwise suitable for growing food crops. Prominent examples explored below include palm oil, jatropha, salicornia, and microalgae, although there are others.

The oil palm, illustrated in Figure 4.5, is a native of Southeast Asia. It produces a fleshy fruit from which palm oil is derived. The kernel of the palm oil fruit also yields palm kernel oil, which is more saturated than palm oil. The oil palm tree

FIG. 4.5 Oil palm (*Elaeis oleifera*).

grows primarily in Malaysia and Indonesia, although equatorial countries in South America and Africa can grow it as well. Its popularity as a crop has grown in recent years both as cooking oil and as lipid feedstock for biodiesel production. The yield of lipids is more than 5600 L/ha, which is nearly 10 times that of soybeans in terms of both energy yield and biofuel yield. This makes it one of the highest-yielding lipid-based feedstocks currently being grown. The oil palm infrastructure is also well developed; palm oil was used in both food and cosmetics for several decades before it became a popular biodiesel feedstock.

Because it grows in tropical countries, concerns have been raised that rainforests will be cleared to allow plantations of oil palm to be grown. Furthermore, its edible nature raises concerns that its use as fuel will compete with food production in developing regions of the world.

Jatropha, illustrated in Figure 4.6, is a genus of hardy bushes and trees originating in the Caribbean and now spread throughout the tropics that produces seeds containing up to 40% triglycerides. Yields for this inedible oil have been reported to be as high as 1400 L/ha. Jatropha oil has been touted as a solution to concerns about fuel crops competing with food crops because it can be grown on marginal and nonarable lands. Oil from jatropha has been successfully hydrotreated to produce jet fuel that has been certified for flight testing.

FIG. 4.6 Jatropha (*Jatropha curcas*).

Jatropha must overcome several challenges before it can be considered a viable biofuel feedstock. Because it has not been domesticated, yields cannot be satisfactorily predicted. These range from an unacceptable 0.1 ton to an impressive 8 tons of seed per hectare. While its ability to grow under poor agricultural conditions is frequently touted, this does not necessarily mean it thrives under such conditions. Additionally, its long-term impact on soil and the environment has yet to be studied. This has also hindered the ability to make accurate estimates of the production costs of jatropha oil. Whereas crops like corn and soybeans have been extensively bred and genetically engineered to develop highly efficient strains, genetic improvement of jatropha to improve its fuel yield is in the very early stages of research.

Salicornia, shown in Figure 4.7, is an edible, salt-tolerant plant that grows in salt marshes and on beaches. Long used for glassmaking and soapmaking, its seeds contain high levels of unsaturated oil suitable for biodiesel production. Its main advantage over other lipid feedstocks is its extremely high salt tolerance relative to other agricultural plants, which allows it to grow in saline conditions that would be toxic to other major agricultural crops. Field trials have demonstrated that salicornia can thrive in extreme coastal desert conditions using seawater as its only irrigation source. It has been reported to produce greater yields of seeds and biomass under these conditions than soybeans grown under ideal agricultural conditions. Originally conceived as an alternative to soybeans for chicken feed, salicornia's ability to thrive in marginal, nonagricultural lands makes it attractive as a nonfood biomass feedstock. Furthermore, the ability to irrigate it with seawater

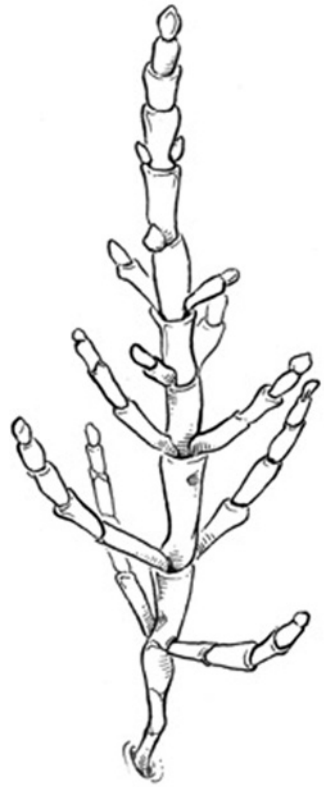

FIG. 4.7 Salicornia (*Salicornia europea*).

provides an opportunity to cultivate dry coastal lands for biofuels production without depleting freshwater sources.

Salicornia faces many challenges similar to those for jatropha. While edible, salicornia has never been domesticated in the same manner as other oleaginous crops, with the result that yields can be attractive but erratic. Furthermore, at roughly 940 L/ha, salicornia's typical yield is far inferior to that reported for jatropha and palm oil (although more than soybeans). There is little data to evaluate the cost of fuel from salicornia.

Microalgae, shown in Figure 4.8, are photosynthetic single-cell microorganisms that grow rapidly under optimal conditions of light and nutrients, producing as much as 100 tons/ha per year of algal biomass containing 5–25% lipid. However, microalgae increase their lipid content when deprived of key growth nutrients such as nitrogen and phosphorus. In this case, lipid content can reach 40–70% although overall biomass productivity generally decreases. As shown in Table 4.1, the potential yield of algae-based fuel is 9800–52 000 L/ha, dwarfing the land

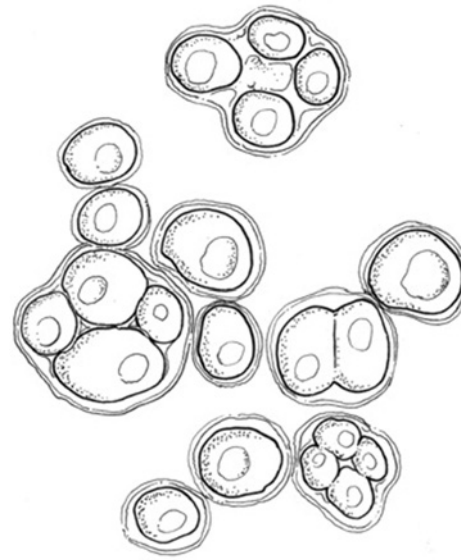

Fig. 4.8 Microphytes.

productivity of biodiesel from sunflower oil and ethanol from cellulosic biomass. Furthermore, algae can be grown on marginal cropland or even within natural bodies of water, allowing it to complement conventional crop production rather than replace it.

The industry faces several hurdles before commercialization. The most formidable is the cost to build the expansive system of ponds or closed reactors that bring together the sunlight, carbon dioxide, water, and nutrients needed to grow microalgae. Open ponds, although little more than concrete or plastic-lined raceways that continuously circulate water and screen out microalgae, are estimated to cost as much as $250 000 per hectare. Photobioreactors are more elaborate closed systems suitable for highly productive pure cultures of microalgae but cost as much as $2.5 million per hectare.

Table 4.1 Comparing biomass yield and fuel productivity for cellulosic and oleaginous feedstocks

Process	Feedstock	Theoretical Fuel Yield (L/ton)	Biomass Production (ton/ha)	Fuel Productivity (L/ha)
Biodiesel	Sunflower	420–520	1.3–3.1	550–1600
Biodiesel	Microalgae	150–420	65.1–124	9800–52 000
Grain ethanol	Corn grain	520	11.2–16.8	5800–8700
Biochemical cellulosic ethanol	Grass	420–470	11.2–44.9	4700–21 000
Thermochemical cellulosic ethanol	Wood	540–670	11.2–44.9	6100–30 000

The major barrier to microalgal fuels is the high cost of microalgal biomass, which at present costs as much as $1000 per dry metric ton—over 10 times the cost of lignocellulosic biomass. The result is algal fuel that costs $20–$75 per gallon. This high cost is largely due to the expense of growing and harvesting microalgae, with feedstock costs being responsible for up to 60% of the cost of algal fuels.

Microalgal biofuels are often touted as a solution to the "food vs. fuel" concern often debated about production of biofuels. Ironically, microalgae could also prove to be an important source of nutrients and dietary protein for direct human consumption or indirectly through its use as animal feed. Microalgae produce large quantities of essential fatty acids (EFAs) such as omega-3, which have been commercially exploited in human nutritional supplements and additives to poultry feed. Algae are also rich in protein that might one day help meet the growing demand for protein around the world although it is not presently palatable as food. Neither are algal fuels a clear solution to land-use concerns. Although microalgae is an aquatic species with potential to be grown in salt marshes or even open oceans, current development focuses on terrestrial systems that would compete with other land uses including irrigated food crops on arid lands that are otherwise fertile.

The harnessing of sunlight and carbon dioxide by plants, protists, and bacteria for growth and production is known as *autotrophic* metabolism. Alternatively, living organisms can obtain essential supplies of energy and carbon from energy-rich organic compounds, a metabolic pathway known as *heterotrophic* metabolism. Many microalgae as well as anaerobic yeasts and fungi can utilize sugars, for example, to accumulate lipids under conditions of nitrogen, phosphate, sulfur, and/or iron deprivation. This eliminates the difficulties of supplying sunlight and carbon dioxide to culture media, reducing capital and operating costs associated with microbial lipid production. However, it does require the production of sugar by conventional agriculture, which reintroduces the issues of competition with food crops.

4.4 Properties of Biomass

Evaluation of biomass resources as potential feedstocks generally requires information about plant composition, heating value, production yields, and bulk density. Compositional information can be reported in terms of organic components, proximate analysis, or ultimate analysis.

Analysis in terms of composition reports the kinds and amounts of plant components including proteins, lipids, sugars, starches, and lignocellulose (fiber). For lignocellulosic crops, engineers are particularly interested in the partitioning among cellulose, hemicellulose, and lignin, while for oleaginous crops the distinction is among carbohydrate, lipids, and protein. Table 4.2 gives the composition of common sugar and starch crops; Table 4.3 includes the composition of several types of

Table 4.2 Composition of starch and sugar crops (dry basis)

Feedstock	Protein (wt%)	Oil (wt%)	Starch (wt%)	Sugar (wt%)	Fiber (wt%)
Corn grain	10	5	72	<1	13
Wheat grain	14	<1	80	<1	5
Jerusalem artichoke	<1	<1	<1	75	25
Sugarcane	<1	<1	<1	50	50
Sweet sorghum	<1	<1	<1	50	50

Source: Wayman, M. and Parekh, S. (1990) *Biotechnology of Biomass Conversion: Fuels and Chemicals from Renewable Resources*. Philadelphia: Open University Press.

dedicated energy crops; Table 4.4 gives the oil content of selected oil seed crops; and Table 4.5 gives the composition of several microalgae species.

Proximate analysis is important in developing thermochemical conversion processes for biomass. Proximate analysis reports the yields (% mass basis) of various products obtained upon heating the material under controlled conditions; these products include moisture, volatile matter, fixed carbon, and ash. Since moisture content of biomass is so variable and can be easily determined by gravimetric methods (weighing, heating at 100°C, and reweighing), the proximate analysis of biomass is commonly reported on a dry basis. Volatile matter is that fraction of biomass that decomposes and escapes as gases upon heating a sample at moderate temperatures (about 400°C) in an inert (nonoxidizing) environment. Knowledge of volatile matter is important in designing burners and gasifiers for biomass. The remaining fraction is a mixture of solid carbon (fixed carbon) and mineral matter (ash), which can be distinguished by further heating the sample in the presence of oxygen: the carbon is converted to carbon dioxide leaving only the ash. Table 4.6 contains the proximate analysis (dry basis) of a wide range of biomass materials.

Ultimate analysis is simply the (major) elemental composition of the biomass on a gravimetric basis: carbon, hydrogen, oxygen, nitrogen, sulfur, and chlorine

Table 4.3 Composition of lignocellulosic crops (dry basis)

Feedstock	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)	Other[a] (wt%)
Bagasse	35	25	20	20
Corn stover	53	15	16	16
Corn cobs	32	44	13	11
Wheat straw	38	36	16	10
Wheat chaff	38	36	16	11
SRWC	50	23	22	5
HEC	45	30	15	10
Waste paper	76	13	11	0

Sources: Bull, S.R. (1991) The U.S. Department of Energy Biofuels Research Program. *Energy Sources*, 13, 433–442; Wayman, M. and Parekh, S. (1990) *Biotechnology of Biomass Conversion: Fuels and Chemicals from Renewable Resources*. Philadelphia: Open University Press.[a]Includes proteins, oils, and mineral matter, such as silica and alkali.

Table 4.4 Lipid content of oil seed crops

Feedstock	Oil Content (%)
Castor	45–50
Corn (germ)	48
Cottonseed	18–25
Jatropha	30–40
Jojoba	45–50
Palm kernel	44–65
Oil palm	30–60
Peanut	45–55
Rapeseed	38–46
Soybean	15–20
Sunflower	25–35

Source: Karmakar, A., Karmakar, S., and Mukherjee, S. (2010) Properties of various plants and animals feedstocks for biodiesel production. *Bioresource Technology*, 101, 7201–7210.

along with moisture and ash. Table 4.6 contains the ultimate analysis of several biomass materials on a dry basis. Sometimes this information is presented on a dry, ash-free (daf) basis. This information is very important in performing mass balances on biomass conversion processes. Evident from Table 4.6 is the relatively high oxygen content of biomass (typically 40–45 wt%).

Of course, from ultimate analyses, the molecular formulas can be worked out. In many instances, a generic molecular formula based on 1 mol of carbon is convenient for performing mass balances on a process. For example, cellulose and starch have the generic molecular formula $CH_{1.7}O_{0.83}$, hemicellulose can be represented by $CH_{1.6}O_{0.8}$, and wood is $CH_{1.4}O_{0.66}$.

Table 4.5 Composition of selected microalgae

Feedstock	Protein (%)[a]	Carbohydrate (%)[a]	Lipids (%)[a]
Anabaena cylindrica	43–56	25–30	4–7
Aphanizomenon flos-aquae	62	23	3
Chlamydomonas reinhardtii	48	17	21
Chlorella pyrenoidosa	57	26	2
Chlorella vulgaris	51–58	12–17	14–22
Dunaliella salina	57	32	6
Euglena gracilis	39–61	14–18	14–20
Porphyridium cruentum	28–39	40–57	9–14
Scenedesmus obliquus	50–56	10–17	12–14
Spirogyra spp.	6–20	33–64	11–21
Arthrospira maxima	60–71	13–16	6–7
Spirulina platensis	46–63	8–14	4–9
Synechococcus spp.	63	15	11

Source: Becker, E.W. (2007) Micro-algae as a source of protein. *Biotechnology Advances*, 25, 207–210.[a]Dry cell weight basis.

Table 4.6 Thermochemical properties of selected biomass

Biomass	HHV (dry) (MJ/kg)	Proximate Analysis (wt%, dry)			Ultimate Analysis (wt %, dry basis)						
		Volatile	Ash	Fixed C	C	H	O	N	S	Cl	Ash
Alfalfa straw	18.45	72.60	7.25	20.15	46.76	5.40	40.72	1.00	0.02	0.03	6.07
Almond shells	19.38	73.45	4.81	21.74	44.98	5.97	42.27	1.16	0.02		5.60
Black locust	19.71	80.94	0.80	18.26	50.73	5.71	41.93	0.57	0.01	0.08	0.97
Cedar (western red)	20.56	86.50	0.30	13.20							
Corn cobs	18.77	80.10	1.36	18.54	46.58	5.87	45.46	0.47	0.01	0.21	1.40
Corn stover	17.65	75.17	5.58	19.25	43.65	5.56	43.31	0.61	0.01	0.60	6.26
Corn grain	17.20	86.57	1.27	12.16	44.00	6.11	47.24	1.24	0.14		1.27
Douglas fir	20.37	87.30	0.10	12.60	50.64	6.18	43.00	0.06	0.02		0.01
Food waste	7.59				17.93	2.55	12.85	1.13	0.06	0.38	5.10
Grape vines		80.10	2.20	17.70							
Hemlock (western)	19.89	87.00	0.30	12.70	50.40	5.80	41.40	0.10	0.10		2.20
Maize straw					47.09	5.54	39.79	0.81	0.12		5.77
Manure (cattle, fresh)	17.36				45.40	5.40	31.00	1.00	0.30		15.90
MSW	19.87	76.30	12.00	11.70	47.60	6.00	32.90	1.20	0.30		12.00
Oak bark	19.47				49.70	5.40	39.30	0.20	0.10		5.30
Orchard prunings	19.05	83.30	2.10	14.60	49.20	6.00	43.20	0.25	0.04		1.38
Ponderosa pine	20.02	82.54	0.29	17.17	49.25	5.99	44.36	0.06	0.03	0.01	0.30
Hybrid poplar	19.38	82.32	1.33	16.35	48.45	5.85	43.69	0.47	0.01	0.10	1.43
Redwood (combined)	20.72	79.72	0.36	19.92	50.64	5.98	42.88	0.05	0.03	0.02	0.40
Refuse-derived fuel	17.40				42.50	5.84	27.57	0.77	0.48	0.57	22.17
Rice hulls	16.14	65.47	17.86	16.67	40.96	4.30	35.86	0.40	0.02	0.12	18.34
Rice straw (fresh)	16.28	69.33	13.42	17.25	41.78	4.63	36.57	0.70	0.08	0.34	15.90
Sorghum stalks	15.40				40.00	5.20	40.70	1.40	0.20		12.50
Sudan grass	17.39	72.75	8.65	18.60	44.58	5.35	39.18	1.21	0.08	0.13	9.47
Sugarcane bagasse	17.33	73.78	11.27	14.95	44.80	5.35	39.55	0.38	0.01	0.12	9.79
Switchgrass	18.64	81.36	3.61	15.03	47.45	5.75	42.37	0.74	0.08	0.03	3.50
Vineyard prunings	16.82				48.00	5.70	39.60	0.86	0.08		1.41
Walnut shells	20.18	78.28	0.56	21.16	49.98	5.71	43.35	0.21	0.01	0.03	0.71
Water hyacinth	16.02		22.40		41.10	5.29		1.96	0.41		
Wheat straw	17.51	71.30	8.90	19.80	43.20	5.00	39.40	0.61	0.11	0.28	11.40
White fir	19.95	83.17	0.25	16.58	49.00	5.98	44.75	0.05	0.01	0.01	0.20
Yard waste	16.30	66.04	20.37	13.59	41.54	4.79	31.91	0.85	0.24	0.30	20.37

Heating value is the net enthalpy released upon reacting a particular fuel with oxygen under isothermal conditions (the starting and ending temperatures are the same). If water vapor formed during reaction condenses at the end of the process, the latent enthalpy of condensation contributes to what is known as the higher heating value (HHV). Otherwise, the latent enthalpy does not contribute and the

Table 4.7 Alkali content of biomass

	HHV (MJ/kg)	Ash in Fuel (%)	Alkali in Ash (%)
Hybrid poplar	19.0	1.9	19.8
Pine chips	19.9	0.7	3.0
Tree trimmings	18.9	3.6	16.5
Urban wood waste	19.0	6.0	6.2
White oak	19.0	0.4	31.8
Almond shells	17.6	3.5	21.1
Bagasse—washed	19.1	1.7	12.3
Rice straw	15.1	18.7	13.3
Switchgrass	18.0	10.1	15.1
Wheat straw	18.5	5.1	31.5

Source: Miles, Sr, T.R., Miles, Jr, T.R., Baxter, L., Jenkins, B., and Oden, L. (1995) Alkali deposits found in biomass power plants. *Summary Report*. National Renewable Energy Laboratory, NREL Subcontract TZ-2-11226-1, April 15.

lower heating value (LHV) prevails. These measurements are typically performed in a bomb calorimeter and yield the HHV for the fuel. Table 4.6 reports HHVs for several biomass materials. Heating values of biomass can be conveniently estimated from the percent of carbon in the biomass on a dry basis using the empirical relationship:

$$\text{HHV in MJ/dry kg} = 0.4571 \times (\%\text{C on dry basis}) - 2.70 \tag{4.1}$$

The inorganic constituents of biomass are important to different extents, depending on the conversion process under consideration. No comprehensive information on inorganic constituents will be provided here, although such information can be found in the literature on biomass. However, knowledge of the alkali metal content of biomass (i.e., potassium and sodium) can be very important if the fuel is to be used in combustors. Experience in burning biomass reveals that excessive alkali salts in biomass, which is particularly concentrated in fast-growing biomass, can lead to ash fouling of boiler tubes. Table 4.7 contains information on alkali in ash for selected biomass materials useful in designing biomass combustion systems.

Bulk density is determined by weighing a known volume of biomass that is packed or baled in the form anticipated for its transportation or use. Clearly, solid logs will have higher bulk density than the same wood chipped. Bulk density will be an important determinant of transportation costs and the size of fuel storage and handling equipment. Volumetric energy content is also important in transportation and storage issues. Volumetric energy content, which is simply the enthalpy content of fuel per unit volume, is calculated by multiplying the HHV of a fuel by its bulk density. Table 4.8 compares bulk densities and volumetric energy contents of various liquid and solid fuels. The cost of collecting large quantities of biomass can be significant. Wood or other biomass resources must generally be

Table 4.8 Density and volumetric energy content of various solid and liquid fuels

Fuel	Density (kg/m^3)	Volumetric Energy Content (GJ/m^3)
Ethanol	790	23.5
Methanol	790	17.6
Biodiesel	900	35.6
Pyrolysis oil	1280	10.6
Gasoline	740	35.7
Diesel fuel	850	39.1
Agricultural residues	50–200	0.8–3.6
Hardwood	280–480	5.3–9.1
Softwood	200–340	4–6.8
Baled straw	160–300	2.6–4.9
Bagasse	160	2.8
Rice hulls	130	2.1
Nut shells	64	1.3
Coal	600–900	11–33

Sources: Grohmann, K., Wyman, C.E., and Himmel, M.E. (1992) Potential for fuels from biomass and wastes, in *Emerging Technologies for Material and Chemicals from Biomass* (eds. R.M. Rowell, T.P. Schultz, and R. Narayan), ACS Symposium Series 476, Washington, DC: American Chemical Society; Larson, E.D., Svenningsson, P., and Bjerle, I. (1989) Biomass gasification for gas turbines power generation, in *Electricity: Efficient End-Use and New Generation Technologies and Their Planning Implications* (eds T.B. Johansson, B. Bodlund, and R.H. William). Lund, Sweden: Lund University Press.

produced within a 50-mile radius of the processing plant to be economical, given the high transportation costs and low densities of biomass.

For many applications, including production of paper and composite materials, the length of fibers in biomass is an important property. Fiber lengths for several kinds of agricultural and forestry biomass are listed in Table 4.9. Extraction of plant fibers is discussed in Chapter 10.

Table 4.9 Dimensions of Some Common Lignocellulosic Fibers

	Fiber Dimension (mm)		
Type of Fiber	Length	Average Length	Width
Cotton	10–60	18	0.02
Flax	5–60	25–30	0.012–0.027
Hemp	5–55	20	0.025–0.05
Manila hemp	2.5–12	6	0.025–0.04
Bamboo	1.5–4	2.5	0.025–0.04
Esparto	0.5–2	1.5	0.013
Jute	1.5–5	2	0.02
Corn stalks	1–1.5	–	0.02
Rice straw	0.65–3.48	–	0.005–0.014
Wheat straw	1.5	–	0.015
Deciduous wood	1–1.8	–	0.03
Coniferous wood	3.5–5	–	0.025

Sources: Rowell, R.M. (1992) *Opportunities for Lignocellulosic Materials and Composites*. ACS Symposium Series 476. Washington, DC: American Chemical Society, pp. 12–27; Rowell, R.M., Young, R.A., and Rowell, J.R. (eds) (1997) *Paper and Composites from Agro-Based Resources*. Boca Raton: CRC Press.

4.5 Yields of Biomass

Planning a biomass conversion facility requires estimates of the total amount of land that must be put into production of biomass crops and how far crops must be transported to a facility. Thus, the annual yield of biomass crops (kilograms per hectare) is important information for an engineer working on such a project. Unfortunately, yield information does not lend itself to tabulation, since it depends on so many variables: plant variety, crop management (fertilization and pest control), soil type, landscape, climate, weather, and water drainage. Table 4.10 has been included to give an idea of the kinds of yields that might be expected in various geographical locations for carbohydrate-rich biomass crops that have been widely studied. Site-specific information will require discussions with state extension agents and local agronomists in combination with field trials in advance of detailed plant design.

Yields of agricultural residues, which are rich in lignocellulosic biomass, are conveniently tabulated in terms of residue factors, defined as the ratio of dry weight of residue to the grain weight at field moisture. Thus, the weight of residue available per hectare of crop can be estimated by multiplying the residue factor by the grain yield in kilograms per hectare. Average residue factors are tabulated in Table 4.11.

Yields of lipid (liters per hectare per year) from terrestrial oil crops are tabulated in Table 4.12. These include conventional oil seed crops like soybeans as well as unconventional crops like jatropha and salicornia. Table 4.13 lists biomass productivity ($g/m^2/day$) for various species of microalgae along with their lipid content and the resulting lipid productivity (L/ha/yr). Of course, these yields

Table 4.10 Nominal annual yields of carbohydrate-rich biomass crops[a]

Biomass Crop	Geographical Location	Annual Yield (kg/ha)
Corn: grain	North America	7000
Corn: cobs	North America	1300
Corn: stover	North America	8400
Jerusalem artichoke: tuber	North America	45 000
Jerusalem artichoke: sugar	North America	6400
Sugarcane: crop	Hawaii	55 000
Sugarcane: sugar	Hawaii	7200
Sugarcane: bagasse (dry)	Hawaii	7200
Sweet sorghum: crop	Midwest	38 000
Sweet sorghum: sugar	Midwest	5300
Sweet sorghum: fiber (dry)	Midwest	4900
Switchgrass	North America	14 000
Hybrid poplar	North America	14 000
Wheat: grain	Canada	2200
Wheat: straw	Canada	6000

Source: Wayman, M. and Parekh, S. (1990) *Biotechnology of Biomass Conversion: Fuels and Chemicals from Renewable Resources*. Philadelphia: Open University Press.[a]Includes moisture content at harvest unless otherwise noted.

Table 4.11 Agricultural residue factors for various grain crops

Crop	Residue factor[a]
Barley	1.5
Corn (<95 bushels/acre)	1
Corn (>95 bushels/acre)	1.5
Cotton	1.5
Oats	1.4
Rice	1.5
Rye	1.5
Sorghum	1.5
Soybeans	1.5
Wheat, spring	1.3
Wheat, winter	1.7

Source: Heid, W.J., Jr. (1984). Turning Great Plains crop residues and other products into energy. Agricultural Economic Report No. 523. Washington, DC: US Department of Agriculture.[a]These factors are ratios of dry weight of residue to the grain weight at field moisture.

exclude coproducts of lipid extraction, which are rich in protein and carbohydrate (see Table 4.5).

Manure is a relatively small biomass resource compared to dedicated energy crops or agricultural residues. However, growing concerns about the environmental impact of manure from large concentrations of animals in many modern agricultural operations make manure a potential biomass resource. Manure production rates for various kinds of livestock and poultry are listed in Table 4.14.

4.6 Size of Resource Base

The amount of biomass that could be produced annually in the United States is difficult to estimate. In addition to the uncertainties in estimating yields on

Table 4.12 Lipid yields for selected terrestrial oil crops

Common name	Species	Lipid yield (L/ha)
Castor bean	*Ricinus communis*	1413
Corn (germ)		172
Chinese tallow tree	*Sapium sebiferum*	6300
Jatropha	*Jatropha curcas*	1900
Jojoba		1800
Palm oil	*Elaeis oleifera*	6000
Peanut	*Arachis hypogaea*	1100
Safflower	*Carthamus tinctorius* L.	600
Salicornia	*Salicornia europea*	940
Soybean	*Glycine max*	450
Sunflower	*Helianthus annuus*	950

Source: Karmakar, A., Karmakar, S., and Mukherjee, S. (2010) Properties of various plants and animals feedstocks for biodiesel production. *Bioresource Technology*, 101, 7201–7210.

Table 4.13 Biomass and lipid productivity for selected microalgae species

	High Growth Condition (Optimal Nutrients Supply)			High Lipid Condition (Nutrient Deprived)		
Marine and Freshwater Microalgae Species	Lipid Content (%)	Biomass Productivity ($g/m^2/day$)	Lipid Productivity (L/ha/yr)	Lipid Content (%)	Biomass Productivity ($g/m^2/day$)	Lipid Production (L/ha/yr)
Ankistrodesmus spp.	24	17.4	16 400	31	11.5	14 000
Botryococcus braunii	25	3	2900	75	3	8800
Chlorella emersonii	25	0.97	950	63	0.91	2300
Chlorella vulgaris	5	0.95	190	58	0.57	1300
Chlorella spp.	10	16.5	6500	48	1.6	3000
Nannochloropsis spp.	12	5.3	2500	53	1.9	4000
Nitzschia spp.	16	21.6	13 600	47	8.8	16 300
Phaeodactylum tricornutum	18	21	14 900	57	2.4	5400

Source: Adapted from Mata, T.M., Martins, A.A., and Caetano, N.S. (2010) Microalgae for biodiesel production and other applications: a review. *Renewable and Sustainable Energy Reviews*, 14, 217–232.

the wide diversity of landscapes that could be planted to biomass crops, a variety of social, political, economical, and environmental factors influence decisions on putting land into biomass production. Since these factors are not static, assessments of land available can change with time. It is not surprising that there is a wide opinion on the size of the biomass supply.

Two studies in the 1990s illustrate the divergence of these views. Graham published an analysis of potential biomass supply in 1994 that foresaw 159 million hectares of land suitable for dedicated energy crops. Since "suitable" was defined as lands capable of producing in excess of 11.2 Mg/ha/year of dry biomass, the total supply of biomass was projected to be 1.8 billion Mg of dry biomass. Assuming heating value of 18 MJ/kg, this analysis, which ignores the contribution of agricultural residues to biomass supply, yields 32 billion GJ of energy (note: in the United States, the unit of national energy consumption is the quad, which is 1 quadrillion British Thermal Units (BTU), equal to 1.054 billion GJ). In contrast, a study by Wyman and Goodman a year earlier estimated dedicated energy crops could

Table 4.14 Livestock and poultry manure generation rates

Animal	Manure Production Rate (dry kg/head-day)
Cattle	4.64
Hogs and pigs	0.56
Sheep and lambs	0.76
Chickens	0.040
Turkeys	0.101

Source: Stanford Research Institute (1976) An evaluation of the use of agricultural residues as energy feedstock, Vol. 1. National Science Foundation Report NSF/RANN/SE/GI/18615/FR/76/3. Washington, DC: National Science Foundation.

supply 26–52 billion GJ of energy. They included agricultural residues, forestry residues, and MSWs in their analysis, which contributed another 8 billion GJ of biomass energy, yielding a total annual energy supply from biomass of up to 60 billion GJ. Since energy consumption in the United States is about 98 billion GJ per year, the Graham study suggests that biomass could supply up to 33% of US energy demand while the Wyman and Goodman study places this percentage as high as 60%.

In 2005, the United States Department of Agriculture sponsored a study of biomass supply, including both dedicated crops and agricultural residues. This study concluded that in excess of 1.2 billion tons of dry biomass, representing 25 billion GJ of energy could be produced in a sustainable manner. In 2011, this comprehensive report was updated to include more rigorous production models and in-depth costs analyses. It also included impacts of land-use change and competition among food, feed, and energy crops in the availability of biomass supply at $60 per dry ton. Its baseline case projected 1.1 billion tons of biomass available by 2030 and as much as 1.6 billion tons under a high-yield scenario. Since the 2011 USDA report is the most recent and takes into consideration information from earlier studies, it will be examined here in more detail.

In 2012, the harvested supply of agricultural and forestry resources in the United States used as biomass supply was estimated to be 214 million dry Mg in the form of wood residues and pulping liquors from the forest products industry, urban wood and processing residues, fuel wood, and grains (Table 4.15). About 60% of this came from forestry resources vs. 40% from agricultural resources. With an average heating value of 18 GJ/ton, biomass contributed nearly 4 billion GJ to the nation's energy supply, which is only 4% of the total US consumption. This is a small fraction of what could be produced and harvested in a sustainable fashion.

The land base of the United States encompasses nearly 2263 million acres. About 33% is classified as forest land, 26% as grassland pasture and range, 20% as cropland, 8% special uses (e.g., public facilities), and 13% miscellaneous such as urban areas, swamps, and deserts. The USDA study considered how the first three categories of land could be employed in biomass production, carefully excluding

Table 4.15 Current biomass supply in the United States (2012)

	Biomass Supply (Million dry Mg/yr)
Forest resources	129
Agricultural resources	85
Energy crops	0
Biomass total	214

Source: US Department of Energy (2011) *U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry*, R.D. Perlack and B.J. Stokes (Leads), ORNL/TM-2011/224. Oak Ridge, TN: Oak Ridge National Laboratory. Available on the web at: https://bioenergykdf.net/

inaccessible and environmentally sensitive lands from consideration. It also accounted for use of these lands in the production of conventional forest products and agricultural commodities.

The study included some forward-looking projections on agricultural technology for its baseline analysis including: corn yields increase by a little more than 1% per year, while energy crop yields increase by 1% per year; harvest technology recovers 60% of crop residue for moderate-yield acres and 70% for high-yield acres; no residue is recovered from soybean crops; there is a continuation in current trends toward no-till and reduced tillage methods; up to 63 million acres of cropland and pastureland are shifted into bioenergy crops by 2030 under a farm gate (undelivered) price scenario of $60 per dry ton; and manure from large and medium livestock operations, as classified by the US Environmental Protection Agency, is used for bioenergy.

Table 4.16 summarizes the findings of the USDA study, which projects 1.1 billion Mg of dry biomass could be harvested annually in the United States by 2030 under an assumed farm gate price of $60 per dry ton. Forestry resources, in the form of fuel wood, milling residues, urban wood residue, logging residues, and wood recovered from forest thinning (for forest fire control) could yield 328 million Mg of dry wood per year or 30% of the total. Agricultural resources, in the form of crop residues, dedicated energy crops, grains for biofuels, processing residues, and manure, could yield 768 million Mg of dry biomass per year. Agricultural biomass and wastes (mostly crop residues) and dedicated energy crops each represent 37% of the total biomass supply. A more optimistic analysis, based on faster gains in crop yields over two decades, suggests that US biomass supply could be as high as 1.6 billion Mg.

Assuming an average heating value of 18 MJ/kg, the base case of 1.1 billion Mg of biomass represents 19.3 billion GJ of energy, or 20% of the total US energy consumption. Calculating the potential for biorenewable resources to replace imported petroleum resources is difficult because, as will become apparent

Table 4.16 Projected biomass supply in the United States (2030)[a]

	Biomass Supply (million dry Mg/yr)
Forest resources currently used	226
Forest biomass and waste resource potential	102
Agricultural resources currently used	103
Agricultural biomass and waste resource potential	265
Energy crops	400
Biomass total	1094

Source: US Department of Energy (2011) *U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry*, R.D. Perlack and B.J. Stokes (Leads), ORNL/TM-2011/224. Oak Ridge, TN: Oak Ridge National Laboratory, Available on the web at: https://bioenergykdf.net/

[a]Includes projections for resources currently used and biomass and waste resource potential that would be available at $60/dry ton.

Table 4.17 Annual livestock and poultry manure generation in the United States

Animal	Population (10^6)	Production (10^6 dry ton)	Heating Value (GJ/dry ton)	Energy potential (10^9 GJ)
Cattle	92.6	157	15.73	2.47
Hogs and pigs	64.9	13.3	16.99	0.226
Sheep and goats	8.5	2.5	17.82	0.0446
Chickens	8660	126	13.53	1.70
Turkeys	246	9.7	13.49	0.131
Total	–	–	–	4.57

Sources: Overview of U.S. Livestock, Poultry, and Aquaculture Production in 2010, Animal and Plant Health Inspection Service, U.S. Department of Agriculture, Washington, DC. Available on the web at: http://www.aphis.usda.gov/animal_health/nahms/; manure production rates calculated from Table 3.16; heating values obtained from Stanford Research Institute (1976) An evaluation of the use of agricultural residues as energy feedstock, Vol. 1. National Science Foundation Report NSF/RANN/SE/GI/18615/FR/76/3. Washington, DC: National Science Foundation.

in subsequent chapters, a kilogram of cellulose is not equivalent to a kilogram of hydrocarbon in generating the fuels and chemicals to which we are accustomed. However, even accounting for the lower conversion efficiency of biomass into transportation fuels compared to petroleum, biorenewable resources have the potential for replacing one-third of the 37 billion GJ of petroleum consumed in the United States in 2011.

Table 4.17 separately considers the energy potential of livestock manure in the United States. The total energy potential is 4.6 billion GJ, with 54% and 37%, coming from cattle and chickens, respectively. However, manure is often highly diluted in water and sometimes difficult to recover, reducing its attractiveness as a chemical and energy resource. Changes in the way that manure is collected and stored would be required in some instances.

World supply of biomass is estimated in Table 4.18. China and India together could produce as much as 1.7 billion dry Mg of biomass, while Latin America could produce 1.5 billion dry Mg. Europe, with its high-density population, has

Table 4.18 Projection of world supply of biomass (2030)

Region	Land Cultivated in Energy Crops (Acres, Millions)	Biomass Supply (Billions dry Mg/yr)
USA (2005 USDA study)	74	1.1
USA (2011 USDA study)	63	1.4
Australia	–	<0.004
China and India	212	1.7
Europe	62–222	0.4–1.5
Latin America	299	1.5

Source: Bauen, A., Berndes, G., Junginger, M., Londo, M., Vuille, F., Ball, R., Bole, T., Chudziak, C., Faaij, A., Mozaffarian, H. (2009) *Bioenergy – A Sustainable and Reliable Energy Source – A Review of Status and Prospects,* IEA Bioenergy: ExCo: 2009:06IEA, 107 pp. Available on the web at: http://www.ieabioenergy.com/LibItem.aspx?id=6479

less potential to grow biomass although it could be in the range of 0.4–1.5 billion dry Mg. Although Africa is not included in this table, it also has large biomass potential if modern agricultural policies and practices were widely adopted in sub-Saharan regions of the continent. In fact, some studies suggest that the tropical parts of the world could become net exporters of bioenergy through sustainable agriculture.

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CHAPTER

5

Production of Biorenewable Resources

5.1 Introduction

Biomass is produced through the practice of agriculture, silviculture, and aquaculture. Traditionally, agriculture was considered the cultivation of herbaceous plants primarily for food and animal feed; silviculture, the maintenance of forests, usually on timescales of decades, either for commercial, recreational, or ecological purposes; and aquaculture, the cultivation of marine or freshwater food sources, usually fish or shellfish. None of these terms fully encompasses the activity of cultivating autotrophic life forms as a means of harvesting solar energy for the production of fuels, chemicals, materials, and energy. Commonly the growth and harvesting of terrestrial vascular plants, whether herbaceous, woody, or oleaginous species, is referred to as agriculture, while growth and harvesting of aquatic nonvascular species such as microalgae will be referred to as aquaculture. Productions of herbaceous crops and woody crops are treated in separate sections of this chapter because of the different timescales associated with their cultivation and the different approaches to their mechanized harvest. Production of oleaginous crops focuses on microalgae rather than oil seed crops, because the later closely follows the production of herbaceous crops. This chapter also considers the storage of biorenewable resources and the application of biotechnology to the production of transgenic crops.

5.2 Herbaceous Crops

As described in Chapter 4, herbaceous crops are plants that have little or no woody tissue and the above-ground growth usually lives for only a single growing season. These include annuals, which die at the end of a growing season and must

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be replanted from seed, and perennials, which die back each year in temperate climates but reestablish themselves each spring from rootstock.

Broadly defined, herbaceous crops include grasses, such as switchgrass, sugar cane, and cereals like corn and wheat; pulses, which are the leguminous plants, such as soybeans, lentil, and alfalfa; and tubers, including potatoes, taro, and Jerusalem artichokes. All have potential application as part of dedicated feedstock supply systems. However, most development has centered on grasses, which is also the focus of this chapter.

5.2.1 Site Preparation

Preparation of the growth zone in soil for plant development is known as tillage. Typically, this tillage zone extends 10–90 cm into the soil. The depth of organic matter in the soil defines the tillable zone. Tillage is required in virgin soils to clear it of plant matter for agricultural use. It also may be performed as part of the process of transferring seeds or seedlings into the soil in a manner conducive to healthy growth of the plants. Ideally, the seed bed is stratified, consisting of a base of coarsely loosened soil, a root development zone of porosity conducive to capillary movement of water, a seed bed zone of fine soil to surround the seeds, and an upper zone of small clods to protect the seeds, as illustrated in Figure 5.1. Tillage is also used to control weeds and other pests living in the soil, although chemical means of pest control have largely supplanted mechanical methods of control.

Texture is a way to classify different sizes of particles making up soil. These classifications include clay (particles smaller than 0.002 mm), silt (particles between 0.002 and 0.05 mm), sand (particles between 0.05 and 2 mm), and gravel and cobbles (particles larger than 2 mm). The latter particles are undesirable as they interfere with tillage and retain little organic matter.

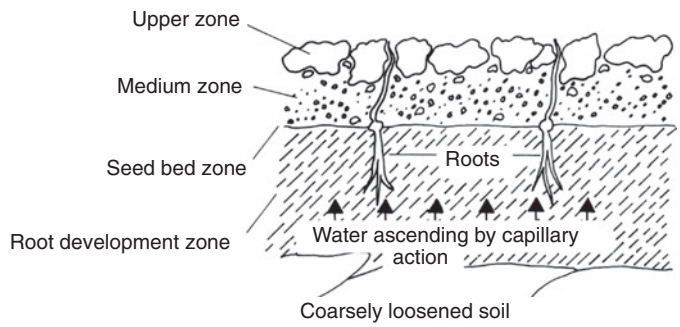


Fig. 5.1 Stratified seed bed of properly tilled soil. Adapted from *CIGR Handbook of Agriculture Engineering, Vol. III: Plant Production Engineering*, B.A. Stout and B. Cheze, eds. St. Joseph, Mich.: American Society of Agricultural Engineers, 1999.

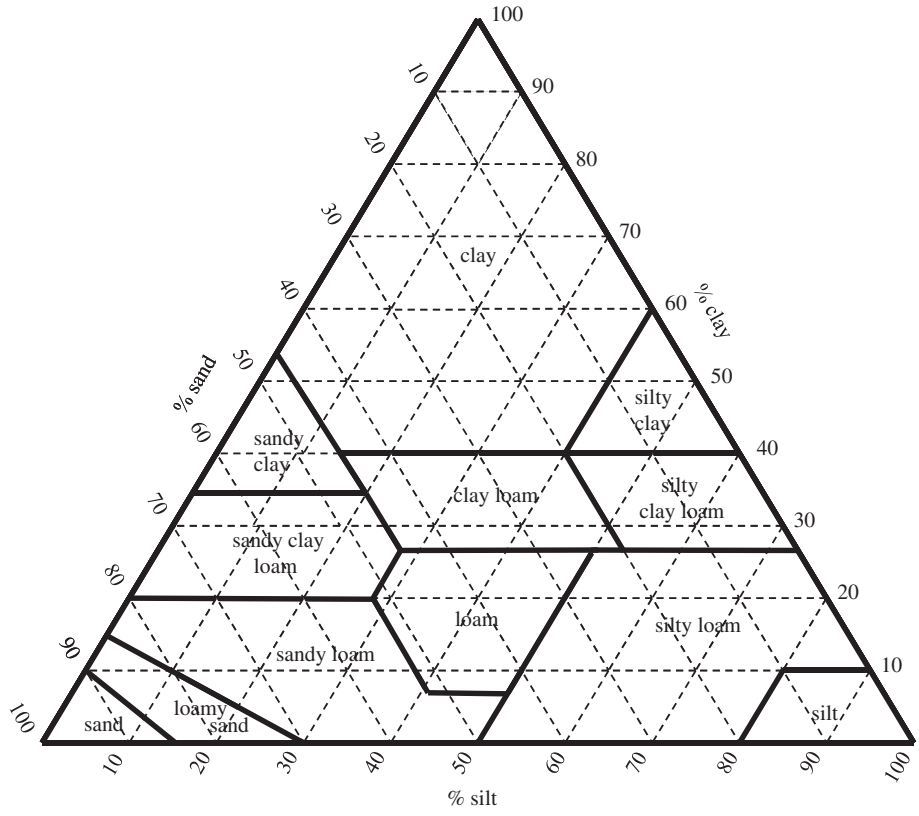


FIG. 5.2 Soil classification triangle. Adapted from *CIGR Handbook of Agriculture Engineering, Vol. III: Plant Production Engineering*, B.A. Stout and B. Cheze, eds. St. Joseph, Mich.: American Society of Agricultural Engineers, 1999.

Soils are classified according to the distribution of the first three size classes (clay, silt, and sand). Soil classifications are represented by the texture triangle shown in Figure 5.2. Soil type greatly influences its workability and suitability for agriculture.

Sands and sand soils, also known as light soils and shown on the lower left hand corner of the texture triangle, are easy to work at all moisture levels. However, water storage capacity is low while infiltration rate and water conductivity are high. This is an advantage for irrigated soils, as salt does not accumulate. Crop yields for sand soils are lower than other types of soils, because organic matter and nutrients are not readily retained.

Silty and loamy soils, also known as medium soils and shown on the lower right hand corner of the texture triangle, are the best agricultural soils. They readily retain water and have porosity suitable for good aeration. They readily retain organic matter and minerals required for good plant growth.

Clay soils, also known as heavy soils and shown on the upper corner of the texture triangle, are difficult to cultivate. At low moisture content they become hard, rendering tillage very difficult. At high moisture content they become plastic, which makes crumbling almost impossible and requires very high draft forces for tillage implements. Porosity is high, but the pores are so fine that aeration is poor and the contained water is inaccessible to plants.

One of the main objectives of tillage is achieving soil porosity that is conducive to both soil aeration and water accessibility to plants. An optimum tilth is usually obtained when crumbs are smaller than 50 mm and a sufficient number of clods exist to create porosity and protect the land against erosion. In the absence of clods, crumbs are readily broken up by wind and water into silty particles that form surface encrustations upon exposure to water. These encrustations interfere with plant growth. In humid climates, looser soil conditioning helps prevent encrustation and improves aeration. In dry climates denser soil conditioning improves water retention.

Figure 5.3 illustrates three types of tillage systems: conventional tillage, reduced tillage, and no-till. The practice of conventional tillage, characterized by high intensity of soil engagement and inversion of the soil, has rapidly declined in the last 50 years because of concerns about soil erosion. Reduced tillage encompasses a wide variety of cultivating practices that have in common less frequent and less intense tillage of the soil compared to conventional tillage. No-till, made possible

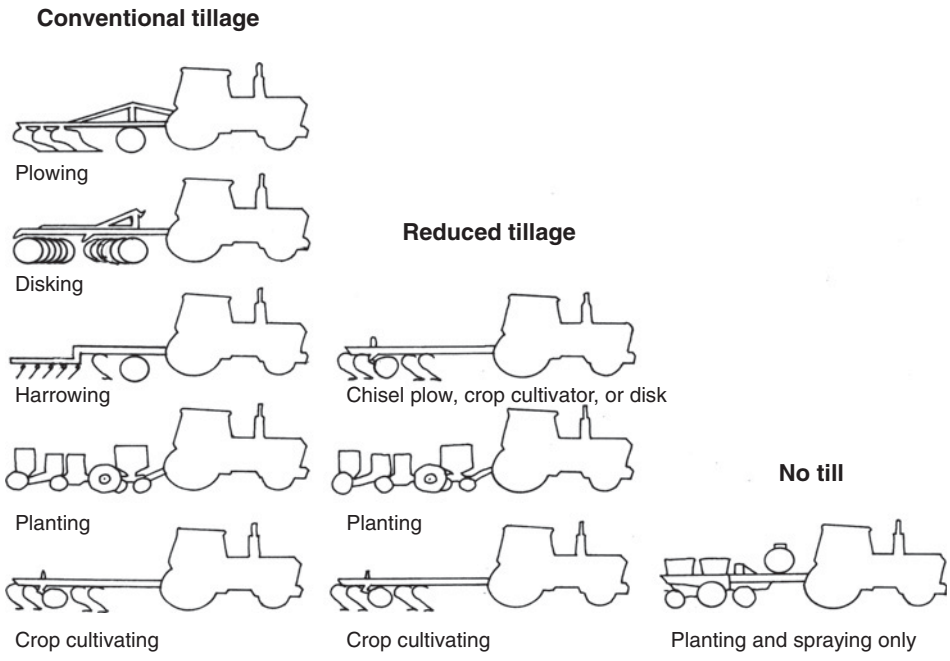


FIG. 5.3 Tillage methods.

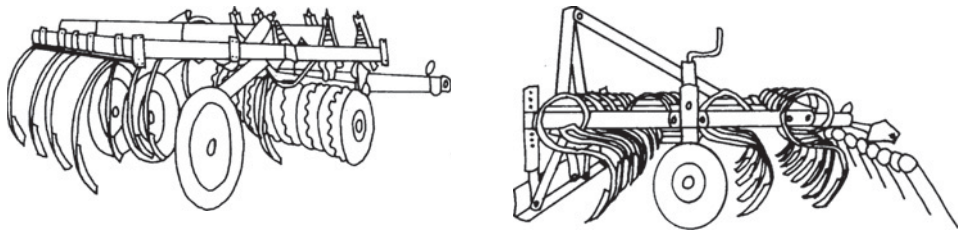
by the development of chemical herbicides, entails very little disturbance of the soil in planting a crop.

Conventional tillage consists of primary tillage followed by several operations of secondary tillage. In heavy soils, primary tillage is accomplished with a moldboard plow. The soil is cut horizontally by a sharp steel element known as a share, and lifted and turned over by a large planar surface known as the moldboard. In arid climates a disk plow is employed, which is less susceptible to obstacles and rough conditions. However, the disk plow is less effective at inverting and crumbling high-organic soils than is the moldboard plow. Primary tillage buries both weeds and plant residues from the previous year's crop. It also produces relatively large soil aggregates; thus, it must be followed by secondary tillage to create a fine seedbed. Among the most common secondary tillage implements is the disk harrow, commonly called a "disk," consisting of several sets of disks on a horizontal axis, angled toward the direction of travel. Dragged over a plowed field, it crumbles, loosens, mixes, and levels the soil into a seedbed. A spiked-tooth harrow, resembling a garden rake in its action, is another implement of secondary tillage.

Reduced tillage is designed to reduce the number of steps in cultivating the soil, with corresponding savings in labor and energy inputs. Some forms of reduced tillage also constitute conservation tillage, which is defined as tillage practices that retain at least 30% of plant residue from the previous year's crop on the surface of the soil. This residue discourages movement of soil by wind and water erosion. Although several different methods of reduced tillage are practiced in different regions of the world, they generally do not employ moldboard or disk plows.

One system of reduced tillage is based on one or two passes of a disk harrow over a field followed by seeding. The greater the disk angle, the greater the degree of soil disturbance and the greater the amount of crop residue that is buried. Generally, not enough residue remains on the soil surface for this method to qualify as conservation tillage.

Another system employs one or two passes of a chisel plow, illustrated in Figure 5.4a. Disk-shaped blades, known as coulters, at the front of the implement cut crop residues, preventing it from plugging the rows of chisels at the back of the



(a) (b)

FIG. 5.4 Reduced tillage implements: (a) stubble mulch chisel plow; (b) spring-tined cultivator.

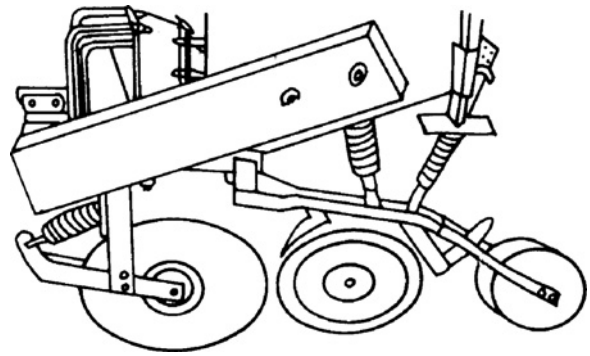


FIG. 5.5 Zero till planter.

implement. The chisel plow cuts the soil to depths of 15–20 cm without burying the entire crop residue. Typically, more than 30% of the residue remains on the soil surface, thus qualifying as conservation tillage. Alternatively, a field cultivator, illustrated in Figure 5.4b, is used in place of the chisel plow or for the second pass over the field after use of the chisel plow. The field cultivator does not cut the soil as deeply as a chisel plow, which helps conserve soil moisture, but it is not as effective in reducing weeds.

Zero or no tillage plants seeds directly into essentially unprepared soil. A typical machine for no till is illustrated in Figure 5.5. This machine cuts a line in the soil for insertion of seeds but does not otherwise disturb the soil. Its success is premised on the use of herbicides to kill weeds before planting.

5.2.2 Seeding and Planting

The final step in planting is insertion of seeds, seedlings, or vegetative propagations into the prepared soil. The term "planter" is used to describe machines that insert seeds into the soil as well as to machines designed for planting seedlings or vegetative propagations.

A simple system of metering a stream of seeds from a hopper through a feeder tube into a furrow is known as bulk drilling and is commonly employed for closely spaced crops such as small grains and grasses. In contrast, widely spaced crops, such as corn and soybeans, are planted using precision drilling, which aims at equidistant spacing of seeds. A modern planter designed to separate seeds for precision drilling is illustrated in Figure 5.6. Drilling depth depends on seed size and water content of the soil: the larger the seeds and the drier the soil, the deeper the seeds are planted to ensure emergence.

The planting of parts of plants, such as potato tubers, and whole plants, such as trees, has also been mechanized. As might be expected, the machines for vegetative

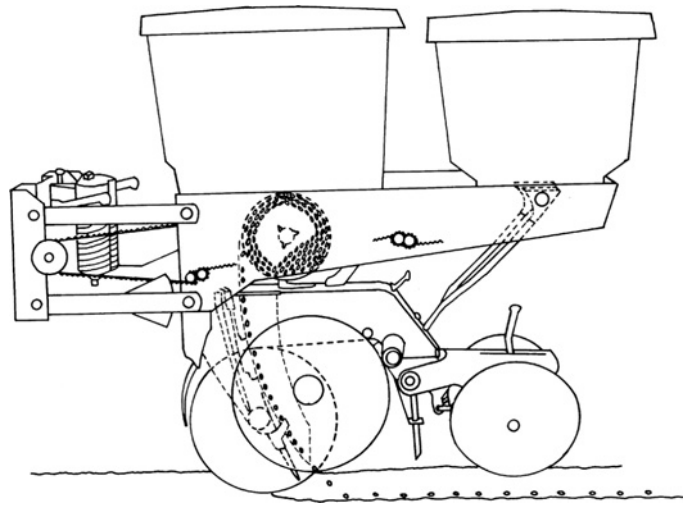


FIG. 5.6 Precision seed drill. Courtesy of Deere and Company.

planting are more complicated than seed planting, and they are designed for specific kinds of plants.

5.2.3 Fertilizer Application

Natural soil fertility declines with crop production, because a large fraction of the biomass is removed from the land, taking with it essential nutrients. Fertilizer is a natural or manufactured material containing high levels of nutrients essential to plant growth. The major nutrients are nitrogen (N), in the form of nitrate, ammonia, or urea; phosphorous (P), analyzed in terms of the P_2O_5; potassium (K), analyzed in terms of K_2O; and calcium (Ca), analyzed in terms of CaO. Although fertilizer requirements vary with soil type and climate, estimated application rates for several biomass crops are listed in Table 5.1.

Fertilizer spreaders are designed for uniform distribution of powdered, granular, or liquid fertilizer, which is critical for optimum performance: either excessive or inadequate application of chemical will reduce crop yield.

A number of distributor types have been developed for powdered and granular fertilizer, including spinning disk spreaders, oscillating spout spreaders, pneumatic spreaders, and auger spreaders. The spinning disk spreaders consist of a conical hopper feeding a spinning disk that is fitted with several radially oriented vanes. Fertilizer falling onto the disks is directed outward along the vanes at velocities of 15–50 m/s, which yields a large broadcast area for the fertilizer. Oscillating spout spreaders consist of a mechanically agitated hopper connected to a spout that vibrates in the horizontal plane. Fertilizer granules are accelerated by the

Table 5.1 Estimated fertilizer requirements for selected crops

	Required Mass Per Unit Weight of Whole Dry Plant, kg/dry ton			
Biomass	N	P_2O_5	K_20	CaO
Alfalfa	0	12.3	34.0	20.7
Corn	11.8	5.7	10.0	0
Kenaf	13.9	5.0	10.0	16.1
Napier grass	9.6	9.3	15.8	8.5
Slash pine (5 year)	3.8	0.9	1.6	2.3
Potato	16.8	5.3	28.3	0
Sugar beet	18.0	5.4	31.2	6.1
Sycamore	7.3	2.8	4.7	0
Wheat	12.9	5.3	8.4	0

Source: Roller, W.L., *et al.* (1975) Grown organic matter as a fuel raw material resource. *NASA Report CR-2608*. Washington, DC: National Aeronautics and Space Administration.

centrifugal forces in the spout, bouncing along the wall a couple of times before being discharged. Pneumatic spreaders entrain granules in a fast-flowing air stream. The air transports the fertilizer through long tubes supported by booms. Deflector plates at the end of the tubes spread the suspension into fans, which provide uniform coverage over the field. Auger spreaders deliver fertilizer from a hopper by means of scrapper floor chains or rubber auger belts to spreading auger booms. They are preferred for application of dusty soil ameliorants, such as potash or ground lime, at high rates.

Liquid fertilizers are of three types: anhydrous ammonia, solution fertilizers, and suspension fertilizers. Although technically more difficult to apply, they have several advantages compared to granular fertilizers including more effective application and the ability to combine fertilizer application with pest control. Because of its high vapor pressure, anhydrous ammonia is injected directly into the soil to prevent its dispersion into the atmosphere. Solution fertilizers consist of soluble fertilizers in water, such as ammonia, urea, or ammonium nitrate. Suspension fertilizers employ a gelling type of clay as an emulsifier to keep finely divided particles of fertilizer in suspension, which is an effective method for applying potassium fertilizer. Both solution and suspension fertilizers can be applied with field sprayers. Directing liquid over spinning fans forms coarse sprays suitable for application to the soil. Liquid nozzles form fine sprays suitable for direct application to plant leaves.

5.2.4 Pest Control

During the growing season, pest control may be required. Pests are anything that impedes or competes with the desired crop and may include weeds, insects, or disease. Control includes mechanical, chemical, and biological methods as well as combinations of these methods known as integrated pest management.

Mechanical weeding removes competing plants from the soil. A number of machines have been developed to support weeding in mechanized farming. The hoeing machine consists of tines or rotary hoes that uproot weeds between rows to a soil depth of 5 cm. The treatment is effective on dry, compact soil and is usually combined with banding application of herbicides. Blade cultivators cut weed roots and rhizomes to a depth of 10 cm by means of horizontal blades mounted on shanks. Brushing machines, effective during early weed emergence, are sets of rotating brushes that uproot weeds between the rows. Chain harrows consist of sets of narrow, flexible, vertical steel spikes that scratch the soil and root out post-emergent weeds from pre-emergent crop or shallow-rooted weeds from amongst deep-rooted crops. The harrow is particularly suited to non-row crops.

Chemical pest control was extensively developed after World War II and is currently the dominant method of controlling weeds, insects, and diseases in crops. Chemical control is classified as either contact or systemic. Contact methods are dependent on local action of the chemical at the point of application, whereas systemic methods are based on absorption and transport of chemicals through the plant to the point of action. The active ingredients of chemical pest control are classified as herbicides, which act against weeds; insecticides, which act against insects; or fungicides, which act against fungi. Dry applications are used where water is scarce or for certain compounds for which powders are more effectively deployed than liquid sprays. Spray applications can be very effective under appropriate meteorological conditions. For example, wind speeds should be below 3 m/s to avoid spray drift, temperature above 10°C promotes leaf absorption, and slight rain or dew improves efficacy of chemical deposition on plant surfaces. A variety of sprayers have been developed including broadcast sprayers, directed or banded sprayers, and in-furrow sprayers.

Biological pest control is of growing interest as a means of reducing the sometimes unfavorable environmental impact of chemical pest control. In this method, fields are deliberately infested with predators and parasites of the pest. The eggs, larvae, or adults of pest predators are mixed with inactive material such as sawdust or hulls and distributed manually by workers walking through the fields to be treated. Because of the multiplier effect of biological pest control (one predator can often consume multiple pests), application rates of the mixtures are low, usually in the range of 5–30 L/ha.

5.2.5 Harvesting

Harvesting is the process of gathering a mature crop from the field. Specific machines have been developed for handling different types of crops: cereals, forage, canes, fruits, nuts, and vegetables. Some of these machines are also able to separate the desired agricultural product from residual plant material (e.g., separating corn kernels from cob, husk, stem, and stalk). In the case of grain crops, this separation

process is known as threshing. A machine that combines both harvesting and threshing of grain crops (cereals) is known as a combine harvester (or simply combine). Since grains and seeds, forage crops, and canes are the agricultural crops of particular interest as feedstocks for biobased products, only harvesting methods appropriate to these three crops will be discussed.

Grain Harvesting

Combine harvesters can harvest a wide variety of grains and seeds, ranging from mustard seeds to broad beans. Combined losses of grain from cutting, threshing, and cleaning can be as low as 1–3%. Mechanical methods have increased productivity of grain harvesting from as little as 10 kg/man-hour in 1800 to 60 000 kg/man-hour today.

The major subsystems of a combine harvester include the gathering and cutting unit (head), the threshing unit, and the cleaning unit. Different kinds of gathering and cutting units are used for different kinds of crops. A head for beans or small grains, illustrated in Figure 5.7, cuts and gathers the stalks and pods with a cutter bar and rotating reel. A head for corn strips the cob from the stalk, leaving the majority of the plant in the field while sending the cob into the combine for further processing.

The crop is conveyed to the threshing unit, which detaches the grain from the ears or pods by a combination of impact and rubbing. Two types of threshing units are available: a cylinder/walker combination and a rotary feeder/separator. The cylinder/walker combination passes the cobs or pods between a cylinder and a concave, illustrated in Figure 5.7, which releases grain to a grain auger while straw enters the straw walker. The straw walker agitates the straw, sifting out grain and chaff not separated in the thresher. The rotary feeder/separator uses a large rotating shaft mounted with tines that both convey the crop through the combine and separate grain from cobs or pods. The straw drops out of the back of the

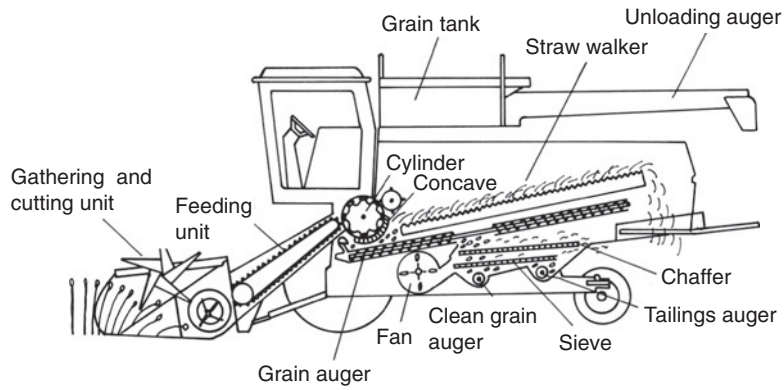


FIG. 5.7 Combine harvester. Courtesy of Deere and Company.

machine and is left in a windrow for later baling, or is baled directly by a baling attachment or press, or is scattered over the ground by a fan-like straw spreader.

Grains, as well as chaff and fragments of straw shaken out of the straw, fall into a grain auger where they pass to the main cleaning device, called the cleaning shoe. The cleaning shoe consists of one or two winnowing steps and two or three oscillating sieves. A winnowing step blows air across grain and material other than grain (MOG) as they fall from the end of the grain pan: chaff and pieces of straw are blown away while the grain falls onto a sieve (or a second grain pan, if there are two winnowing steps). The combined action of sieve oscillation and classification by airflow allows grain to penetrate the MOG layer and fall through the sieves to a grain auger which transports it to a grain tank. Material rejected by the top sieve is thrown from the back of the harvester, while material rejected by the bottom sieve(s), which may still contain significant grain, is returned to the threshing unit by a tailings return system. Correct adjustment of the air blast, by adjusting fan speed, throttling the intake of the fan, or by altering the setting of baffles, is important in determining the degree of cleaning of the grain and the magnitude of the grain losses that occur.

Forage Harvesting

Forage crops are classified according to the method by which they are ultimately prepared for storage: hay and silage. The various crops used for these different preservation methods are listed in Table 5.2. Hay is preserved by storing at low moisture levels. Both grasses and legumes are harvested, as hay with alfalfa being the most common hay crop. Silage is preserved at high moisture levels by fermenting it in the absence of oxygen, which produces organic acids that kill microorganisms that cause spoilage. Corn is most commonly employed as a silage crop. Haylage is a lower moisture version of silage, which further promotes preservation by limiting oxygen during storage. Distinctive methods of harvesting and storage are employed for these two kinds of forage crops. Hay is usually harvested in operations requiring several passes over the field, whereas silage or haylage crops are often collected in a single pass.

Table 5.2 Forage crops classified according to preservation method

Preservation Method	Crop
Hay	Alfalfa, clover, sorghum, birdsfoot trefoil, reed canary grass, smooth bromegrass, Bermuda grass, wheat grass, Canada wild rye, timothy, Russian wild rye, native grasses, cereal grains
Silage or haylage	Corn, forage sorghum, sudan grass, sorghum-sudan hybrids, oats, alfalfa, alfalfa–grass mixtures

Source: Cavalchini, A.G. (1999) Forage crops. In: *CIGR Handbook of Agricultural Engineering, Vol. III: Plant Production Engineering* (eds B.A. Stout and B. Cheze), pp. 350–374. St. Joseph, MI: American Society of Agricultural Engineers.

Since hay harvesting does not involve separation of plant parts, equipment much simpler than combined harvesting and threshing machinery can be employed. For haymaking, this involves separate steps of cutting the crop (mowing), conditioning the cut crop to improve field drying (tedding), arranging the crop into long rows in the field (windrowing), and either baling the crop or loading the loose hay into wagons. The main parameters associated with the various operations of haymaking are summarized in Table 5.3.

Mowers include rotary mowers, which cut by means of impact forces, and cutter bars, which apply shearing forces to cut the plant material. Rotary mowers have high cutting speeds (10–12 km/h) and working widths of 1.5–3 m. However, they consume 20–25 kW-h/ha, which is about 40% higher than cutter bar mowers. Cutter bar mowers employ either an oscillating knife working in combination with a fixed finger bar or a mechanism of dual oscillating elements. The former cutter bar mechanism is the more robust of the two and is better suited for cutting crops close to the ground. Cutter bar mowers have mowing speeds of 8–12 km/h and working widths of 1.5–2.5 m. Energy consumption is 18–20 kW-h/ha.

Mowers often incorporate a mechanical treatment known as conditioning, which improves the uniformity of drying time for coarse stems and fine leaves. This not only slightly reduces field-drying times but also, more importantly, prevents delicate leaves from overdrying and being lost during windrowing and baling. Conditioners can increase nutritive value of forage crops by as much as 15%. Conditioners consist of rollers for legumes or flails for grasses that slightly crush plant stems, which allows more rapid release of moisture from this coarse plant part.

As part of haymaking, after the crop is cut and partially dried in the field, it is turned and fluffed to promote additional drying. This process, known as tedding, was traditionally performed with a pitchfork. Modern machinery performs this operation by means of flexible forks on rotors mounted on a vertical axis: the forage is lifted off the ground and pitched backwards.

Windrower rakes distribute the cut crop into long rows in the field as a prelude to baling or collecting the material. Modern side delivery rakes include parallel-bar rakes and finger wheel rakes, illustrated in Figure 5.8, as well as rotary rakes. Although an apparently simple operation, the ability to efficiently rake cut forage without contaminating it with soil while operating on irregular terrain is difficult to achieve. Leaf loss is a strong function of moisture content of the crop, ranging up to 8% loss for moisture content below 30%. Large, self-propelled windrowers produce a loose, fluffy windrow, which makes tedding unnecessary. Machinery has also been developed that combines mowing, tedding, and windrowing in a single operation.

Early methods of haymaking produced piles of dry, loosely consolidated plant material known as haystacks. Mechanization allowed hay to be compressed into rectangular bales of 15–30 kg weight that were easy to handle and store, helping

Table 5.3 Unit operations of haymaking

Operation, Machine	Speed (km/h)	Average Working Width (m) or Volume (m^3)*	Capacity (ha/h,m) or (t/h)	Minimum Power (kW)	Energy Consumption (kW-h/ha) or (kW-h/t)*	Time (man-h/ha) or (man-h/t)*
Mowing:						
Walking mower (finger bar)	2–3	1.2–1.4	0.2–0.25	8	18–20	4–5
Finger bar mower	5–7	1.5–2.5	0.4–0.5	15	18–20	0.8–1.6
Double knife cutter bar	6–9	1.5–2.5	0.5–0.7	15	18–20	0.6–1.2
Rotary disc mower driven from below	9–10	1.5–3.0	0.7–0.8	25	20–25	0.5–1.0
Rotary drum mower from the top	10–12	1.5–2.5	0.8–0.9	30	20–25	0.6–0.9
Tedding: rotary tedder	10–14	2–6	1.5–6	20	10–15	0.2–0.7
Windrowing:						
Rotary rake	7–9	3–6	0.3–0.4	25–30	18–20	0.6–1.5
Parallel bar rake	6–7	2–3	0.25–0.35	15–20	15–18	1.0–2.0
Finger wheel rake	6–8	2–5	0.25–0.35	15–20	15–18	0.7–2.0
Mowing + Windrowing:						
Rotary drum mower driven from the top	10–12	1.5–2.0	0.8–0.9	30	20–25	0.6–0.9
Loading:						
Forage self-loading wagon	4–6	1.2–2.0 15–30*	0.6–1.2 15–20*	30	15–20	0.8–1.5
Baling: conventional baler	4–6	1.0–1.8	2–8	25–45	1.8—2*	0.13–0.5*
Round baler	5–7	1.5–2.0	2–8	40–60	2.0–2.2*	0.13–0.5*
Big baler	6–8	1.8–2.2	10–15	70–100	1.9–2.1*	0.07–0.1*
Stack-wagon	4–6	1.6–2.0	10–15	40–70	1.5–1.8*	0.007–0.1*

Source: Cavalchini, A.G. (1999) Forage crops. In: *CIGR Handbook of Agricultural Engineering, Vol. III: Plant Production Engineering* (eds B.A. Stout and B. Cheze), p. 354. St. Joseph, MI: American Society of Agricultural Engineers.

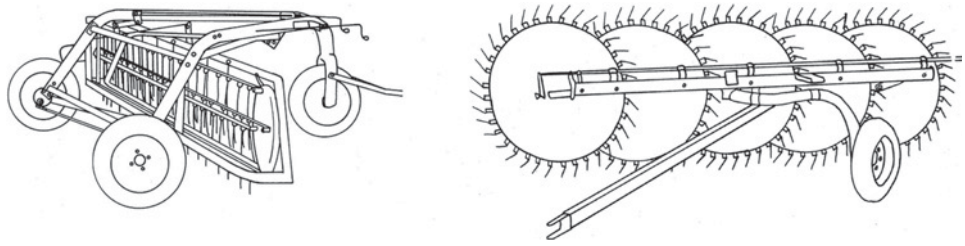


FIG. 5.8 Two types of hay rakes: (a) parallel-bar rake; (b) finger wheel rake. Courtesy of Deere and Company.

reduce the labor for forage harvesting from 40 man-hours/ha to 20 man-hours/ha. However, with continued mechanism of agriculture, this conventional bale proved to be a bottleneck to further productivity improvements in haymaking. Modern handling systems include development of big bales and round bales, weighing as much as 700 kg, and systems for collecting loose hay in self-loading wagons or stack wagons. Pelletizing or cubing of forage to high densities (approaching 450 kg/m^3) has been explored as a means of facilitating handling and storage. Although technically feasible, the approach has only limited commercial application because of high capital costs as well as energy costs in the range of 25–30 kW-h/t.

Figure 5.9 illustrates a big baler. Compression is usually achieved in two phases: in a prechamber, the forage is accumulated and partially pressed followed by final compaction in the upper compression chamber. In the upper chamber a plunger compresses the bales to densities in the range of 180–230 kg/m^3. Five to six binders are applied to hold the bale together. The bale length of 2.4 m is comparable to the length of trucks designed to haul them. Offsetting the high collection rate of 15 t/h or higher are high power requirements of the baling machine.

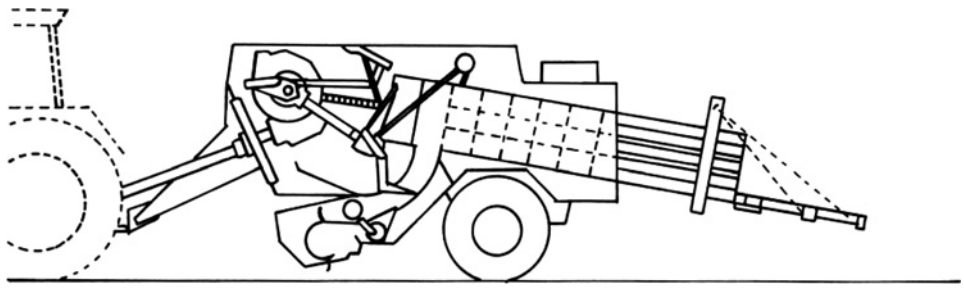


FIG. 5.9 Rectangular big baler. Adapted from *CIGR Handbook of Agriculture Engineering, Vol. III: Plant Production Engineering*, B.A. Stout and B. Cheze, eds. St. Joseph, Mich.: American Society of Agricultural Engineers, 1999.

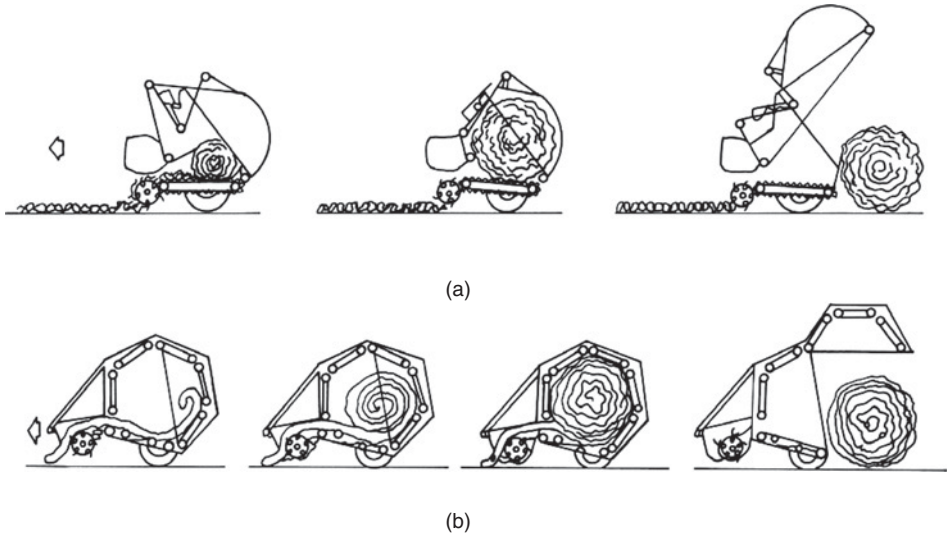


FIG. 5.10 Two kinds of round balers: (a) variable chamber, core compacted; (b) fixed chamber, loose core. Adapted from *CIGR Handbook of Agriculture Engineering, Vol. III: Plant Production Engineering*, B.A. Stout and B. Cheze, eds. St. Joseph, Mich.: American Society of Agricultural Engineers, 1999.

Figure 5.10 illustrates the two kinds of round balers: loose core and compact core. The loose core baler forms the bale in a chamber of fixed volume, which permits the bale to form around a relatively fluffy center with the periphery becoming more compact as the chamber fills. The disadvantage of reduced density is offset by greater air circulation within the core, which promotes additional drying without heat buildup after baling. The compact core baler employs a variable volume compression chamber, which provides constant compression during the accumulation of hay in the chamber.

Some parts of the world use self-loading wagons, illustrated in Figure 5.11, to harvest hay. They consist of a trailer with high sideboards and a cylinder type pickup combined with a forage chopping system. The chopping system produces lengths of hay that are 20–40 cm long for barn drying and 8–10 cm long for silage.

Stack wagons produce a fairly compact haystack of density between 100 and 150 kg/m^3 with sloping top able to shed rainfall. The wagons, pulled by a tractor, have flail type pickups consisting of horizontal rotors with flails or knives attached, which apply shearing forces on the forage. The forage is kicked up and transported pneumatically to a large, rectangular compression chamber constructed of sheet metal. The top surface is a movable canopy that allows the load to be compressed as the chamber is filled. Stack wagons are often employed to create winter feed stores left on the field. The storage density and volume, bale weights, tractor power and

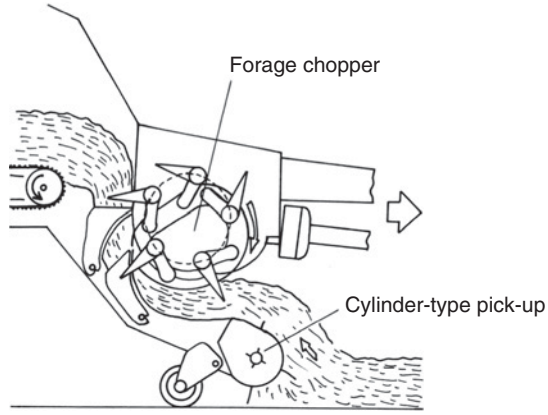


FIG. 5.11 Self-loading wagon for hay harvest. Adapted from *CIGR Handbook of Agriculture Engineering, Vol. III: Plant Production Engineering*, B.A. Stout and B. Cheze, eds. St. Joseph, Mich.: American Society of Agricultural Engineers, 1999.

energy requirements, and collection rates for these various options are summarized in Table 5.4

Forage cereals, by virtue of their high-soluble sugar content, must be ensiled for successful storage. Thus, harvesting occurs at relatively high moisture content, in the range of 32–38% depending on the kind of cereal. Forage harvesters can either collect windrowed material or cut a standing crop. Forage heads include windrow

Table 5.4 Characteristics of different hay collection methods

Collection Method	Hay Density (kg/m^3)	Bale/Stack Dimension or Wagon Volume		Weight (kg)	Energy Requirement (kW-h/t)	Collection Rate (t/h)
Self-loading wagon	<100	10–20 m^3		1000–3000	1–1.2	4–4.6
Stack wagon	100–150	Length (m)	2–5	1000–6000	1.5–1.8	10–15
		Width (m)	2–3			
		Height (m)	2.5			
Conventional bale	125–165	Length (m)	0.7–1.2	15–30	1.5–2.5	4–8
		Width (m)	0.40–0.5			
		Height (m)	0.35–0.45			
Big bale	180–230	Length (m)	1.0–2.4	200–700	2–2.5	10–20
		Width (m)	0.8–1.2			
		Height (m)	0.5–1.0			
Round bale	130–205	Length (m)	1.0–1.8	200–700	2–2.5	4–12
		Dia. (m)	1.0–1.8			

Source: Cavalchini, A.G. (1999) Forage crops. In: *CIGR Handbook of Agricultural Engineering, Vol. III: Plant Production Engineering* (eds B.A. Stout and B. Cheze), pp. 350–374. St. Joseph, MI: American Society of Agricultural Engineers.

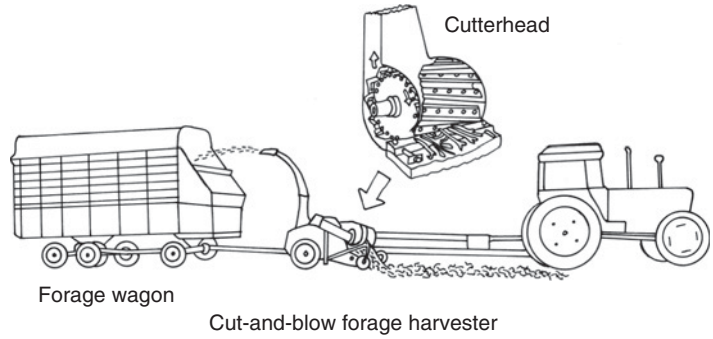


FIG. 5.12 Basic forage harvester operation. Courtesy of Deere and Company.

pickup for haylage, mower bar for winter cereals or standing grasses, and row crop for corn silage. The forage is then fed to cutterheads, illustrated in Figure 5.12, that chop the forage to suitable size, typically 6–9 mm for maize and winter cereals and 20–30 mm for grasses.

Machinery is being developed for the simultaneous harvest of corn grain and stover. Conventional combine harvesters collect the grain and leave stalks, leaves, husks, and cobs, collectively known as stover, in the field. If stover is to be harvested, a second pass over the field is required. A more economical approach to the collection of clean stover is to pick it up at the time the grain is harvested. Gathering heads have been adapted to combine harvesters that process the whole plant, sending the stover to a storage bin separate from that for grain. These systems show promise in producing stover free of dirt and containing essentially all the cobs. The amount of residues left on the field can be adjusted according to local soil conservation needs.

Cane Harvesting

Sugar cane can be harvested either as whole cane, the traditional method of harvesting, which can be done either manually or mechanically, or as chopped cane, which was developed for harvesting by power-driven equipment. Whole cane harvesting is practiced where labor is inexpensive or where a gradual transition to mechanization is desired to prevent disruptions in existing harvesting and processing infrastructure. It also produces a very clean crop, important in fiber production. Chopped cane harvesting reduces multiple steps of traditional harvesting into a single machine. Early attempts to adapt machines to local climate and geography have been abandoned in favor of field and crop management practices that are conducive to mechanical harvesting, such as leveling ground and growing lodging-resistant varieties of sugar cane.

Manual cutting of whole cane involves three operations: cutting the cane at the base; trimming off the top; and laying the canes in windrows or heaps. Loading the windrowed or heaped canes onto wagons for transport completes the harvest. Mechanization of whole cane cutting imitates one or more operations of cutting, trimming, and windrowing. Some machines simply cut the cane and require follow-up by human laborers or machines, while other approaches completely mechanize the cutting operations. Loading of either windrowed or heaped cane is performed discontinuously with front-mounted tractor loaders, self-propelled front-end loaders, swivel loaders, or power loading trailers. Windrowed cane allows the option of continuous loading by means of wide chain elevators that pick up the whole canes, chop them into 40–50-cm lengths with circular saws, and drop them into a following wagon.

Chopper harvesters completely mechanize the harvesting operation, including the loading of cane into a trailer. The cane is cut at the base, chopped into 20–40-cm lengths, and loaded directly into a trailer. The cane can be chopped immediately after cutting, which is known as "bottom chopping" (i.e., near the ground), or after it is conveyed through the machine, which is known as "top chopping" (i.e., elevated from the ground). The advantage of bottom chopping is reduced power requirement by the machine. The advantage of top chopping is that cutting blades are protected from dulling by soil and rocks.

The method of transporting cane to sugar mills depends on the distance involved. Field tractors and trailers are frequently used for distances of less than 10 km. High-capacity road trailers or tractor trailers are used for longer distances. Occasionally, private rail systems are employed for large production systems. In any case, cut cane must be delivered to the mill and crushed within 25 hours if the field was burned before harvest, or within 48 hours if cut green to prevent sugar loss.

5.3 Woody Crops

The term short rotation woody crop (SRWC) is used to describe woody biomass that is fast growing and suitable for use in dedicated feedstock supply systems. Desirable SRWC candidates display rapid juvenile growth, wide site adaptability, and pest and disease resistance. Promising tree species include poplar (*Populus* spp.), willow (*Salix* spp.), silver maple (*Acer saccharinum*), sweet gum (*Liquidambar styraciflua*), sycamore (*Platanus occidentalis*), black locust (*Robinia pseudoacacia*), and *Eucalyptus* spp. Trees of potential regional importance in the United States include alders (*Alnus*), mesquite (*Prosopis*), and the Chinese Tallow (*Sapium sebiferum*).

Hybrid poplar and eucalyptus are most promising for the United States because of high growth rates ranging between 20 and 43 Mg/ha/year. In the United States,

hybrid poplar has a wider range than eucalyptus, which is limited to southern Florida, California, and Hawaii. Hybrid poplar is also attractive for the ease of propagating it from either stem cuttings or tissue culture.

5.3.1 Site Preparation

Short rotation woody crops need to be established under conditions similar to those for herbaceous crops. Deep, well-drained fertile soils with adequate rainfall provide the best yields. Light textured soils such as sandy loams or silty loams are preferred, but heavier textured soils can be employed with sufficient drainage. Thus, suitable acreage ranges from good cropland to land that is marginal for conventional crop production because of poor drainage or erosion potential.

Although hybrid poplar may have the best overall potential for dedicated feedstock supply systems, other species are better adapted to certain regions or marginal lands. Sycamore and sweet gum are more suitable for Southeastern United States where respiration rates are higher and drought more common. Silver maple is well adapted to bottomlands susceptible to flooding, while black locust, which can extract nitrogen from the atmosphere (nitrogen fixation), can be grown on nutrient-poor soils. SRWCs are unsuitable for cutover upland forest sites because of generally thin soils, low fertility, and susceptibility to erosion.

Site preparation should begin 1 year before planting. Abandoned cropland or pasture typically requires brush removal, mowing, plowing, and application of broad-spectrum herbicide to eliminate competing plants. Conversion of row-crop fields to SRWC may only require a single spring plowing and row-marking operation. Conventional farm tractors and implements, such as moldboard plows, discs, and harrows, can be used for site preparation.

5.3.2 Seeding and Planting

Seeding is not directly employed to establish trees in dedicated feedstock supply systems. Instead, bareroot seedlings, containerized stocks, or cuttings are planted in the prepared site. Large-seeded species can be sown in beds where they sprout and grow into seedlings that are transplanted as bareroot seedlings. Containerized stocks are trees grown in plastic or fiber pots, which generally produces trees with higher survival rates upon field planting than do the alternative propagation methods, but at a cost that is 25–250% higher than the alternatives. Cuttings are plants reproduced by clonal propagation, a process by which the tissue taken from the root, stems, or leaf of a plant is grown into a whole plant that is genetically identical to the original plant. Clonal propagation is favored for dedicated feedstock supply systems, because trees with the most desirable properties, such as disease resistance or rapid growth under specific local site conditions, can be selected and rapidly multiplied.

In some instances, clonal propagation requires culturing the vegetative tissue in special "cloning solutions" until roots are established at which point the cutting can be planted to the field or a container. However, cuttings from many hardwood species can be planted directly into the ground. Most planting material is a 25-cm-long hardwood cutting with diameters of 1–2 cm. Species that sprout and grow readily include many *Eucalyptus* spp., *Populus* spp., and *Chlorophora excelsa*.

Spacing of plantings is critical as it affects establishment costs, optimal rotation ages, and tree size at harvest. Optimal spacing is a function of the tree species, soil quality, climate, and desired size at harvest. Narrow row spacing has the advantage of allowing tree crowns to shade out competing weeds within 3 or 4 years and reducing branching. Tree spacing ranges from 1×1 m^2 for willow plantations that are harvested every 2–3 years (10 000 trees per hectare) to 4×4 m^2 for large saw logs (625 trees per hectare). Planting densities of 1500 trees/ha might be considered typical. Both hand planting, at rates of 4 ha/day/person, and machine planting, at rates of 16 ha/day for a three-person crew, have been employed. Machine planting can be problematic in rocky soils, wet soils, or poorly prepared soils.

5.3.3 Fertilizer Application

Fertilization is required to maintain rapid growth rates as well as maintain the fertility of the soil. For trees planted to fertile bottomlands, application of fertilizer may not be required until the second rotation of SRWC. Most sites will require nitrogen application by the third year. Granular nitrogen fertilizer can be applied by either ground or aerial equipment. Ground application of granular nitrogen is done with cyclone-type applicators.

5.3.4 Pest Control

Good survival and growth of SRWC can be achieved compared to either HEC or conventional crops if the site is thoroughly prepared and planted with fast-growing clones. Herbicide applications before and after planting are usually employed to reduce labor of hand and mechanical weed control. Rotary hoes can be used to till newly established plantations on light (sandy) soils to control emerging weeds until the trees are 30 cm tall.

A large number of animal and microbial pests must also be controlled. These include deer, elk, beavers, voles, and gophers in the first two years of establishment and insect and fungal species in even well-established stands. The best strategy is to select species and clones that are best adapted to pests indigenous to the region. For example, hybrid poplar is a poor choice for eastern United States because of insect and fungal pests. In some circumstances, application of insecticides or fungicides may be required to control these pests.

5.3.5 Harvesting

Rapid juvenile growth and high carbon sequestration rates can be sustained only if the stands are regularly harvested. Typically, rotations are no longer than 8–10 years as growth rates peak after 4–6 years and quickly slow as a result of competition among the trees.

Harvest should occur during the dormant season, which allows significant translocation of nutrients to the roots or returned to the soil by leaf fall. This assures rapid growth of coppice the following spring. There is little data on long-term productivity of SRWC grown in coppice systems. Some economic analyses project that stands will be harvested only three times, representing a total time period of 15–30 years before they are replaced with improved tree varieties.

Harvesting equipment for traditional logging operations was developed for broken terrain typical of upland forests as opposed to the relatively flat agricultural lands to be planted to SWRCs. Much of it is adapted for coniferous (softwood) trees that are larger and less uniform than the deciduous (hardwood) trees of interest for dedicated feedstock supply systems. Thus, an evolution of harvesting equipment can be expected for woody crops as the industry develops.

Harvesting in the near term will employ several pieces of machinery familiar to the conventional logging industry. A feller/buncher, illustrated in Figure 5.13, performs the initial operation of cutting the trees (felling) and stacking them (bunching). The self-propelled machine, which is either rubber-tired or tracked, has an articulated, extensible arm at the end of which is a felling head. The felling head consists of a grappling device and either a disc or a chain saw. The human operator uses the grappling device to grasp the trunk of a single tree or possibly the trunks of up to six small trees. The saw severs the tree trunk from the stump, and the operator maneuvers the articulated arm to rotate the trunk to a horizontal position and lay it into a pile of felled trees.

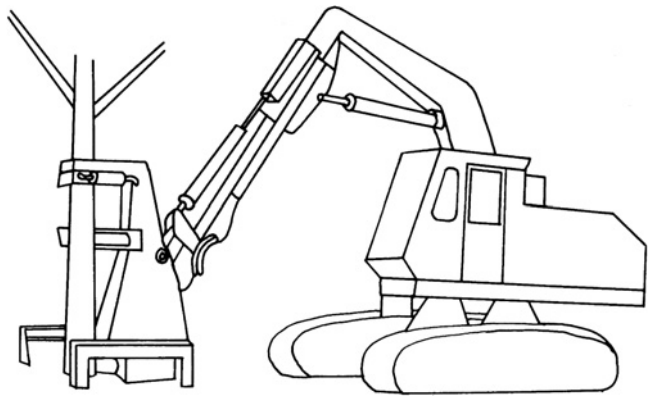


FIG. 5.13 Feller/buncher for cutting and piling woody crops.

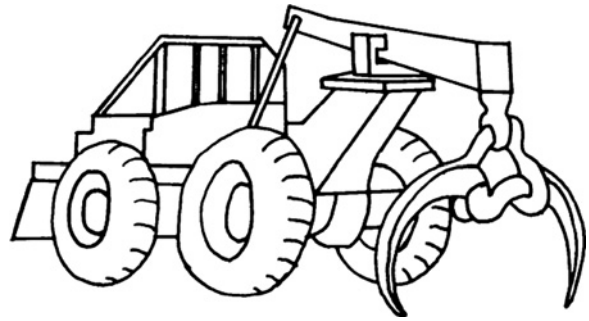


FIG. 5.14 Grapple skidder for moving piles of felled trees to a "landing" for further field processing.

A grapple-equipped skidder, illustrated in Figure 5.14, transfers the pile of felled trees to a centralized "landing" for further processing. The grapple skidder is a rubber-tired, four-wheel drive vehicle with a dozer blade on front and a maneuverable grappling device on the back. The skidder is backed into position next to a pile of trunks and the grapple used to pick the pile off the ground before transporting it to the landing.

At the landing, limbs and bark are removed mechanically usually by a flail, which is a rotating drum fitted with lengths of steel chain that batter the tree trunks, breaking off limbs and shattering bark. The mixture of bark and limb wood is usually suitable only as fuel wood. The delimbed and debarked tree trunks are then feed to a tub grinder, also located at the landing, which produces chipped pulpwood suitable as feedstock in processing to chemicals or fibers. The combined operations of delimbing, debarking, and chipping are illustrated in Figure 5.15.

Flail delimbing and debarking is the bottleneck in producing clean feedstock from woody crops. High production rates yield unacceptably high levels of bark

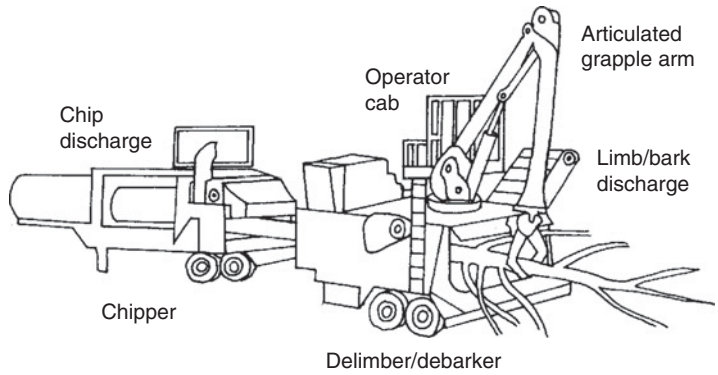


FIG. 5.15 Flail delimber/debarker/chipper operation.

mixed with the pulpwood, which must be less than 1% to be suitable. Furthermore, the process entails relatively high operating costs, including energy consumption (40–70 MJ per dry Mg of residues) and chain replacement.

Equipment optimized for harvest of SWRCs are still being developed. Some of these resemble the mechanical harvesters that are used to cut and collect bundles of sugar cane stalks. Others are essentially heavy-duty forage harvesters like those used to chop corn stalks into silage except with larger cutting heads. This development will probably proceed slowly until widespread commercial markets develop for the pulpwood.

5.4 Production of Oleaginous Species

As described in Chapter 4, oleaginous species are very diverse, ranging from oil seed crops like soybeans to nonvascular (typically aquatic) species like microalgae. The methods for cultivating and harvesting oleaginous crops are just as diverse. For more exotic oleaginous crops, such as salicornia, these methods have not been well established.

Rather than presenting a comprehensive review of cultivation and harvest of oleaginous crops, this section focuses on microalgae, which have the greatest potential for large-scale production of lipids for processing into fuels and chemicals. Readers interested in oil seed crops should refer to Section 5.2 of this chapter for a description of cultivating and harvesting grain crops, which utilize similar methods and equipment.

5.4.1 Microalgae Cultivation

Most schemes for large-scale autotrophic cultivation of microalgae, whether marine or fresh-water species, are envisioned to be land based using specially constructed open raceway ponds or closed tubular photobioreactors (PBRs). Open raceway ponds, illustrated in Figure 5.16(a), are shallow, oval-shaped containments split in the middle to allow water to be circulated around them, usually by the action of a paddle wheel. Raceway ponds may encompass 300–4000 m^2 with an average depth of 20–30 cm. Carbon dioxide and nutrients are injected into the pond to encourage high microalgae productivity, which is typically in the range 5–35 $g/m^2/day$. Evaporation from the open ponds can help moderate heat gain associated with absorption of sunlight, but this also exacerbates water loss. Phase change liquids are sometimes floated on the surface of the ponds to reduce both water loss and heat gain. Raceway ponds have the advantage of simple design and construction. Because they are open to the environment and prone to contamination, neither conventionally bred nor genetically modified organisms can be cultivated in raceway ponds, which would be outcompeted by wild strains of algae.

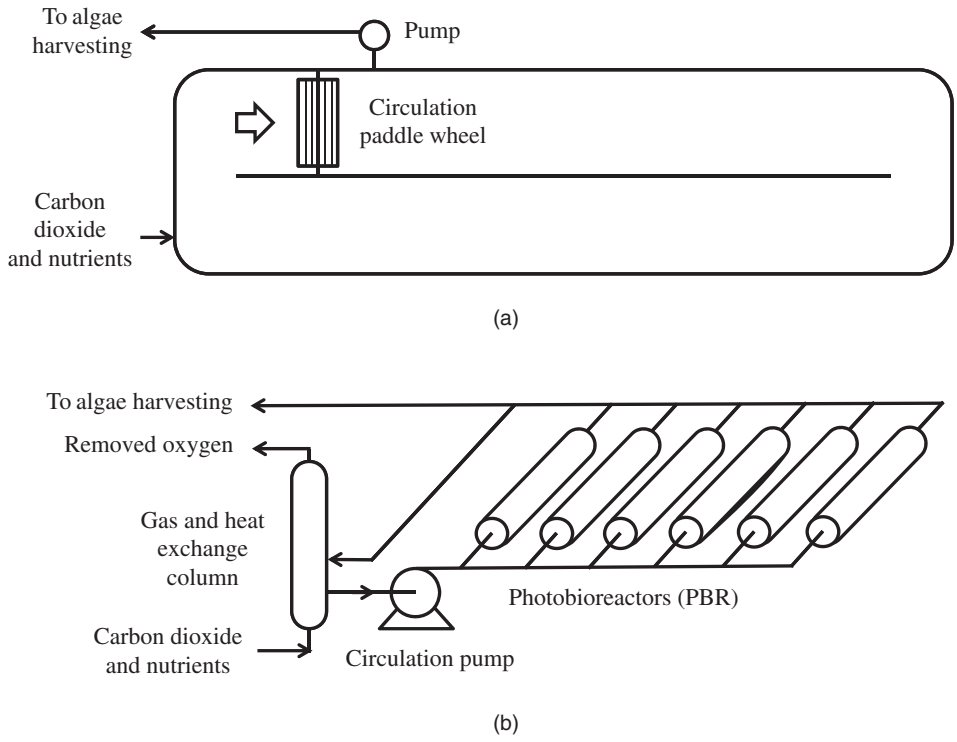


FIG. 5.16 Algae cultivation systems: (a) open raceway pond (top view); (b) closed PBRs.

Tubular PBRs, illustrated in Figure 5.16(b), are usually installed horizontally, although some pilot-scale reactors are installed at an angle to the horizon to improve solar insolation. The diameter of the tubes is about 10 cm. A pump continuously moves water and suspended algae through the reactors, heat exchangers, and gas exchangers. If properly designed, algae productivity can be 14–48 g/m^2/day. Compared to raceway ponds, closed tubular PBRs have the advantages of lower contamination risk, less water loss, almost no carbon dioxide loss, less complicated process control, reduced susceptibility to weather, and land requirements that are only 30% of that of open raceway ponds. On the other hand, they have increased risks of overheating and excessive dissolved oxygen levels. The greatest disadvantage is their high construction costs, which can be 10 times higher than for open raceway ponds.

Another possibility for growing microalgae is open ocean cultivation in regions of the world known as high nutrient, low chlorophyll (HNLC) areas. These regions have sufficient nutrients to support the growth of algae or other aquatic species except for the absence of certain micronutrients, especially iron. Some researchers have proposed fertilizing HNLC regions with iron, which would promote rapid

growth of autotrophic microorganisms. Although originally proposed as a way to promote ocean photosynthesis for the purpose of sequestering carbon from the atmosphere, the biomass could be harvested for bioenergy production instead of sequestering it in the ocean. Limited experimental trials have proven that ocean fertilization can enhance photosynthesis, but the environmental impacts have not been sufficiently evaluated and harvesting microalgae in the open ocean would be challenging.

5.4.2 Microalgae Harvesting and Water Removal

Harvesting microalgae involves unique challenges compared to harvesting vascular plants. Optimal growth requires low algae concentrations in water (about 50 mg/L or, on a mass basis, 500 parts per million) and continuous harvesting. On the other hand, processing of biomass requires solids loading of at least 20–30 wt% (wet processing) or even moisture contents as low as 10–15% (dry processing). Methods for recovering microalgae and removing water ahead of processing are still under development, but resemble in many respects those used in wastewater treatment. Solids recovery is often conducted in stages, incrementally decreasing the moisture content of the microalgae. These stages, illustrated in Figure 5.17, include screening, thickening, dewatering, and drying.

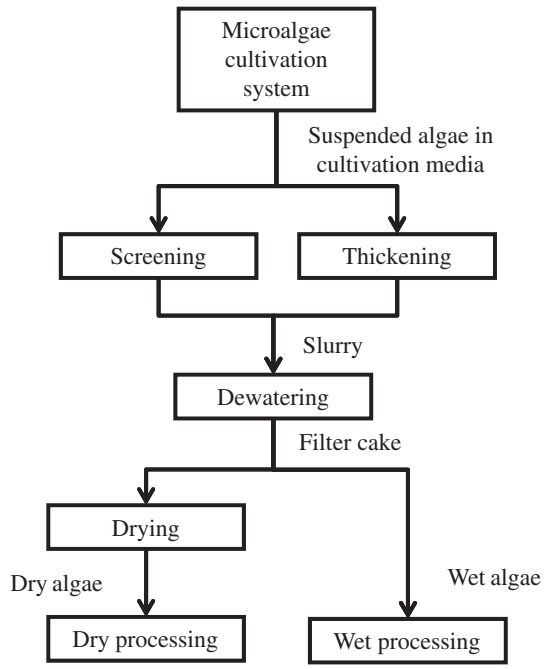


FIG. 5.17 Flow diagram for algae harvesting and solids recovery.

Screening, when employed, is the first operation in solids recovery with the goal of increasing solids concentration two orders of magnitude above the typical 0.05% solids concentration of the microalgae growing in water. Although able to process large volumes of water at relatively low cost, success is dependent upon screen apertures being smaller than the size of the microalgae. For some microalgae species, with cellular diameters as small as 5–10 μm, this can be challenging. Screening can remove up to 95% of the microalgae suspended in water and yield algal slurry containing 6–10% solids.

Thickening is an alternative to screening. Thickening can be achieved through several techniques including gravity sedimentation, flocculation, and flotation. Gravity sedimentation simply transfers the cultivation media to a quiescent settling tank or basin and allows suspended algal cells to settle out by the action of gravity. Flocculation is the process of encouraging single cells of algae to agglomerate into large cell masses (flocs), which can occur naturally or by the addition of chemicals. Clearly, flocculation would increase the ease and efficiency of screening or the speed of gravity sedimentation. Flotation is used for very light suspended particles, which do not readily settle by gravity. Air bubbles are admitted to the bottom of the flotation tank, which attach to the algae and make them light enough to float to the surface where they accumulate, allowing them to be readily skimmed off. Flocculation can increase the efficiency of flotation.

Dewatering has the goal of sufficiently reducing the water content of slurries produced by thickening to be handled as a solid, sometime known as filter cake. Dewatering, possibly occurring in stages, typically increases solids content from 2–10% to 12–35%. Major dewatering operations include several kinds of filtration and centrifugation. Filtration, in contrast to the removal of solids from water by screening, is the removal of water from solids. Filtration can be either surface or deep granular bed phenomena. In either case, some kind of backwash or granular media cleaning must occur periodically to sustain the process. Different kinds of filtration include pressure filtration, vacuum filtration, granular bed filtration, magnetic filtration, and cross-flow ultrafiltration. Centrifugation involves imparting high centrifugal forces on the algal slurry, causing separation between the denser solids and the lighter water. Several variations of centrifugation have been developed, including solid-bowl decanter centrifugation, nozzle-type centrifugation, and solid-ejecting disc centrifugation. Dewatering, although relatively low energy compared to drying, consumes significant power to develop the pressures or velocities required for their effective operation. Dewatering consumes as much as 40% of the total power required to grow, harvest, and process algal biomass.

Drying is the application of heat to filter cake to reduce moisture content to the range of 10–15%. The decision to dry the biomass depends upon whether dry or wet processing is desired. These alternative processing approaches are discussed in Chapter 9. Since the starting moisture of filter cake is usually on the order of 80%, significant heat energy is required to dry it. When employed, drying constitutes

70–75% of the processing cost. The kind of drying method employed depends on the scale of the operation and the ultimate use of the dried product. The major classes of drying equipment include direct-fired rotary dryers, steam-heated rotary dryers, spray dryers, cross-flow dryers, and vacuum-shelf dryers.

5.5 Storage of Herbaceous and Woody Biomass

Agricultural production is seasonal, with crops being harvested only once or just a few times per year, while processing to energy, fuels, chemicals, or materials is a year-round activity since manufacturing facilities are too expensive to remain idle most of the year. Most biomass undergoes substantial degradation in the course of a few months or even days if exposed to the elements after harvest. Accordingly, proper storage to preserve plant materials for periods of a year or even longer is critical to the successful development of a biobased products industry. Traditional methods of long-term storage involve drying, cooling, or ensiling a crop or immediately processing the crop to obtain a more stable intermediate product. Each has its advantages and disadvantages, the choice depending on the nature of the crop and the kind of processing it will ultimately undergo.

5.5.1 Drying

Drying removes moisture from a crop to the levels that impede growth of microorganisms. Freshly cut biomass may have a moisture content of 60% or higher for woody biomass and 70–85% for herbaceous biomass. This moisture exists in two forms: free water within the pores of the plant material and bound water absorbed in the interior structure of the material. Successful preservation of plant material may require drying to as little as 10% moisture. Drying is a very energy-intensive process, theoretically requiring 2442 kJ of energy for every kilogram of moisture removed at 25°C. Actual drying, which is often performed at temperatures slightly higher than 100°C, requires about 50% more thermal energy than this theoretical level to account for sensible heat of both the biomass and the air used for drying. To dry a ton of biomass containing 50% moisture to 10% moisture would require about 1.5 GJ of energy, representing about 18% of the energy content of the fresh biomass. Thus, field drying is employed whenever possible.

A crop left standing in a field beyond maturity will naturally dry, as is commonly done for such crops as corn, soybeans, and wheat. Green crops can also be cut and left lying in the fields to dry, as is commonly practiced in haymaking. The level of drying depends upon the climate, the kind of crop, and the structure of the plant part. For example, leaves dry more readily than stems and plant parts protected by pods or husks will dry more slowly than exposed plant parts. In many regions of the world, grasses can be field dried to moisture levels consistent with long-term

storage. Many grains, though, protected as they are by pods and husks, require additional drying in grain silos after they have been harvested, depending on local climatic conditions.

Barn drying of hay is employed in climates where field drying is not practical. After the forage is cut, it is allowed to field dry down to a moisture content of 40–45%. The material is then collected with a self-loading wagon as previously described and stored in a drying barn where either ambient air or air that has been heated 10–20°C above ambient is circulated through the hay to reduce the moisture to around 15%. Barn drying is often employed in small to medium dairy farms.

Baling, as previously described, is appropriate for hay and crop residues, such as corn stover. Conventional balers do not yield sufficient compaction for economic storage, especially for stalks. Large round or square bales are more appropriate for long-term storage. Large round bales can be stored outside for several months, but there can be some losses due to water damage and weathering. Bales can also be wrapped in polyethylene sheets, canvas, or nylon tarpaulins for field storage, which helps shed water. Ideally, bales are stacked in sheds to protect them from the weather. Handling of baled crops is very labor intensive, which makes this mode of storage unattractive in places where development has increased the cost of labor.

5.5.2 Cool Storage

Storing biomass in a cool, dry environment is also an effective method for discouraging microbial degradation. Farmers traditionally used root cellars, consisting of excavations into hillsides, as a cool place to store tubers for periods longer than would otherwise be possible for these relatively high-moisture crops. Today refrigerated rooms are used to store high-value crops, such as seed corn, but use of cool storage is not practical for commodity crops.

5.5.3 Ensiling

Ensiling was developed for humid climates where field drying is impractical, but it is finding increasing application in drier climates. Ensiling is attractive for automating the handling and storage of cereals, grasses and legumes, bagasse, and even cornstover, the latter of which is typically much drier than traditionally ensiled crops. Grasses and other graminaceous species are easier to ensile than legumes, the protein content of which promotes butyric fermentations associated with rotting of the forage.

The crop is ideally harvested at a moisture content of 40–50% and stored under anaerobic conditions to promote partial fermentation of sugars to organic acids, which suspends further microbial degradation of the crop. Chemical additives, usually organic acids, water-soluble salts, or pulverized limestone, are sometimes added for pH control.

Storage systems include horizontal silos and vertical silos. Horizontal silos include bunkers, consisting of an above ground structure of concrete floors and walls; trenches dug into the ground, with either bare earth or concrete floors and walls; large polyethylene bags; and unprotected stacks for temporary storage. Vertical silos include conventional silos, constructed from metal, concrete, or tile, and oxygen-limiting units usually constructed of metal with an inner lining of fused glass. The technology is relatively easy to implement and requires no direct energy input.

Losses during ensiled storage are inevitable. If properly preserved, biomass losses can be kept to only 5–10%, depending upon the sugar content of the ensiled material (e.g., bagasse, the fibrous stalks remaining after expressing juice from sugar cane, has a relatively high residual sugar content). Improper ensiling can result in losses as high as 30%.

5.6 Transgenic Crops

For thousands of years, mankind has employed plant breeding to improve yields of sugars, starch, oil, and protein in crops, increase resistance to pests, and adapt plants to local climatic conditions. In conventional plant breeding, genes already existing within a species are brought together in new combinations by sexual crossing in an effort to express desirable characteristics. Statistical laws control the possible outcomes, but careful selection of offspring with desired traits makes the process deliberate. Recent advances in biotechnology broaden the scope of plant breeding by allowing selection of desirable traits across species, thus the name *transgenic crops*. Because genetic material is directly manipulated, the process is also less probabilistic, the outcomes known a priori.

5.6.1 Genetic Manipulation

The process of creating a transgenic plant, illustrated in Figure 5.18, begins by identifying an organism, whether bacteria, plant, or animal, that contains the desired trait to be expressed in the new plant. The expression of this trait is mediated by various proteins that serve as catalysts for biochemical reactions or as

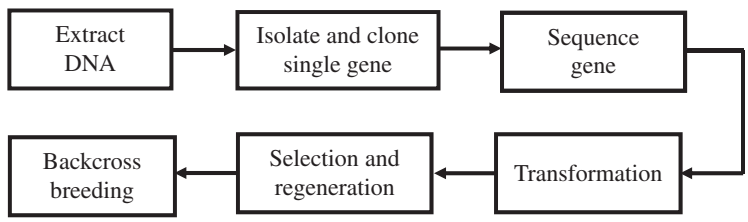


FIG. 5.18 Steps in producing a transgenic plant.

building blocks for cellular components. The genetic roadmap for manufacturing these proteins is the organism's deoxyribonucleic acid (DNA), usually contained within the cell nucleus. Because all organisms employ similar mechanisms for transcribing and translating the information contained in DNA into proteins, the DNA from one organism, in principle, can be inserted and used in another organism.

A gene is a segment of DNA that controls assembly of a particular protein. Thus, after *extracting* DNA from the organism that expresses the desired trait, the next step is to isolate the gene that produces the protein associated with the trait. Although tremendous strides have been made in "mapping" DNA for various organisms, the process of identifying and locating genes for agriculturally important traits will limit the rate of introduction of transgenic crops for several years to come. Usually, it is not enough to know which stretch of DNA produces a particular protein since other genes may also interact with the biochemical pathway to be manipulated. However, once the gene has been identified, it can be *isolated* by the use of restriction enzymes, which recognize and cut phosphate bonds at specific locations along the backbone of the DNA molecule, and further manipulated with ligases, enzymes that join fragments of DNA. The isolated gene is inserted into bacteria where it is replicated, or *cloned*, in sufficient quantities for subsequent genetic manipulations.

The isolated and cloned gene requires further genetic manipulation, called *sequencing*, before it can be successfully expressed as a transgene in a host plant. As shown in Figure 5.19, this entails the addition of a selectable marker gene, a promoter sequence, and a termination sequence. The selectable marker gene is added as a means of identifying which plant cells have successfully integrated the transgene, since the insertion process has a relatively low probability of success. Selectable marker genes encode proteins that confer resistance to agents that are normally toxic to the plant being transformed. For example, the marker gene might protect against an antibiotic or herbicide. Thus, plants that successfully incorporated the transgene are identified by treatment with the toxic agent and selecting the surviving plants. The promoter sequence is the on/off switch that controls when and where the plant gene will be expressed. A "constitutive" promoter is commonly employed, which causes the gene to be expressed throughout the life cycle of the plant in most tissues. Other promoters respond to specific environmental cues, such as light. The termination sequence simply indicates to the cellular machinery that the end of the transgene has been reached.

Transformation is the process of inserting the transgene into the desired host plant. A wide variety of techniques have been developed to achieve

FIG. 5.19 Components of a constructed transgene.

transformation including plant viruses, chemically mediated DNA uptake, *Agrobacterium* cocultivation, electroporation, microinjection, microprojectile bombardment, and electric discharge particle acceleration.

Certain kinds of plant viruses can introduce DNA into normal, healthy plants. Transformation may be as simple as rubbing the leaves of the target plant with viruses in which the transgene has been inserted: the virus systematically infects the cells of the plant, transferring the gene into the plant's genetic material. The most commonly employed viral vector is the cauliflower mosaic virus. Viral transformation is limited to plants that it can naturally infect. They have little prospect for producing transgenic cereal crops.

Polyethylene glycol and polyvinyl alcohol, in combination with calcium ions and high pH, can produce chemically mediated uptake of DNA. The integrated gene was shown to be inheritable in subsequent generations of plants transformed in this manner. Transformation frequency is inferior to other techniques, in particular *Agrobacterium* cocultivation, but may have application to graminaceous monocotyledons (species related to grasses), which are more difficult to transform by *Agrobacterium* cocultivation, as subsequently described.

Agrobacterium cocultivation involves the coincubation of plant cells with *Agrobacterium tumefaciens*, a soil bacterium that naturally infects many dicotyledonous (broadleaf plants like soybeans and tomatoes) and gymnospermous (coniferous) plants. The DNA for this organism is contained in the bacterial chromosome as well as in a structure known as the Ti (tumor-inducing) plasmid. The Ti plasmid includes a section of DNA known as T-DNA, which is transferred to the plant cell during the infection process, and another section of DNA, known as vir (virulence) genes, which directs the infection process. To harness *A. tumefaciens* as a transgene vector, the tumor-inducing section of T-DNA is removed, while the T-DNA border regions and the vir genes are retained. The transgene is inserted between the T-DNA border regions, which is transferred into plant cells during coincubation and becomes integrated into the plant's chromosomes. The process has been widely employed because of the large number of cells that can be treated at a time and the uniform exposure that is achieved. However, many important monocotyledons, such as rice and corn, are not susceptible to transformation by this technique.

Electroporation achieves transformation by applying a high electrical potential to a mixture containing plant cells and the transgene. The process is hypothesized to induce cell membranes to a state of high permeability, allowing transgenes to diffuse into the cells, although the exact mechanism is not fully understood. Electroporation has found application to monocotyledons and other plants that are recalcitrant to other transformation processes. The advantages of this approach include inexpensive instrumentation, reproducibility, and avoidance of toxic chemicals.

Microinjection uses microcapillaries and other microscopic devices to deliver DNA into individual plant cells. The potential for microinjection was first

demonstrated in rapeseed, but the technique has not advanced as much as other transformation processes. As might be expected, the process requires considerable skill and specialized instrumentation, and only one cell receives DNA per injection.

Microprojectile bombardment accelerates micron-sized particles of tungsten or gold that have been coated with DNA to velocities sufficient for nonlethal cell penetration. This "biolistics" approach requires careful refinement to avoid excessive morality of plant cells so treated. This transformation process has been extensively studied, especially for monocotyledonous species such as rice and corn. A closely related process, electric discharge particle acceleration, applies a high-voltage electric discharge to a tiny water droplet, which rapidly vaporizes and serves as propellant to DNA-coated spheres of gold. Uneven particle distribution and cell death by bombardment contribute to low transformation efficiency for these two processes.

From the above descriptions of transformation processes, it is evident that a relatively small fraction of attempts to insert a transgene into plant cells are successful. Accordingly, gene insertion must be followed by *selection and regeneration*, in which plant cells that have successfully incorporated the transgene are separated from the rest of the plant cells and grown into whole plants. The inclusion of a selectable marker gene in the constructed transgene makes this separation possible. The mixture of transgenic plant cells and normal plant cells from the transformation process is transferred to a growth medium containing the toxic agent for which the selectable marker gene affords immunity. Thus, only the plant cells that have successfully incorporated the transgene will survive, all others perish from the toxic agent.

Those plant cells surviving the selection process are grown under controlled environmental conditions in a series of growth media containing nutrients and hormones into whole plants. These whole plants generally do not possess the qualities of modern cultivars demanded by producers and consumers. Therefore, the transgenic plant will be crossed with an improved variety. This initial cross to the improved variety must be followed by several cycles of repeated crosses to the improved parent, a process known as *backcross breeding*. The goal is to recover as much of the improved parent's genome as possible, with the addition of the transgene from the transformed parent.

The final step in the process is multilocation and multiyear evaluation trials in greenhouse and field environments to test the effects of the transgene and overall performance. This phase also includes evaluation of environmental effects and food safety.

5.6.2 Biobased Products from Transgenic Crops

Genetic transformation of crops offers many opportunities for plant improvement, including resistance to herbicides, protection against insects and other pests,

hardiness against frost, and the manufacture of valuable products in plants. This latter prospect has led to discussions about "plant factories" and "plant molecular farming." Biobased products that might be manufactured directly in plants to yield commercially recoverable quantities include antibodies, oligopeptides and proteins, sugar oligomers and polymers, phenolics and alkaloids, essential oils, monomers for biodegradable polymers, and enzymes for industry and therapeutic purposes.

An example of a particularly intriguing prospect is the growth of a class of industrial polymers called polyhydroxyalkanoates (PHA) in plants. This concept was based on the observation that the bacterium *Alcaligenes eutrophus* can directly synthesize poly-3-hydroxybutyrate (PHB), which accumulates as polymeric inclusions in cell bodies, from glucose. However, the relatively high cost of glucose and other suitable carbon sources makes the economics of PHA from bacteria unattractive compared to the polymers derived from fossil resources.

Since plants use carbon dioxide and sunlight for their carbon and energy sources, genetically modifying a plant to produce PHA would appear to be a more economical alternative to manufacture in bacteria. To this end, researchers engineered the enzymes controlling PHB synthesis into *Agrobacterium* plasmid, which was used to genetically transform *Arabidopsis thaliana*, a small flowering plant that is a member of the mustard (*Brassicaceae*) family, to produce polymers in plant tissues. Up to 14% PHB in dry weight of leaves has been achieved. The production of PHAs in plants has yet to be realized, as technical questions remain concerning the separation of polymers from plant tissue and the overall energy requirements of processing facilities.

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CHAPTER

6

Products from Biorenewable Resources

6.1 Introduction

Biorenewable resources can be converted into bioenergy or biobased products. *Bioenergy* includes process heat, biopower, and biofuels; while *biobased products* include chemicals and natural fibers, from which an array of finished products can be manufactured. This chapter is an introduction to these products from biorenewable resources and gives some idea of their use in commercial markets.

Process heat is the thermal energy used to raise the temperature of solids, liquids, or gases for residential, commercial, or industrial applications. It includes heating of homes, firing of bakery ovens, heating water for laundries, drying grain, raising steam for manufacturing processes, melting ores, and a variety of other low- and high-temperature processes. Other than a few instances of solar and geothermal heating, almost all process heat is derived from combustion in air of energy-rich organic compounds like coal, natural gas, or biomass, collectively referred to as fuels. Combustion generally occurs at very high temperatures, which for many applications must be moderated by post-combustion dilution of the resulting flue gas or heat transfer to water or other media.

Biopower is defined as the conversion of biorenewable resources into electric power. It is usually intended to designate energy for stationary applications as opposed to energy for transportation. This distinction is important, as biopower applications typically employ solid or gaseous fuels, whereas transportation applications employ liquid fuels, although there are exceptions to these generalizations.

Biofuels are chemicals derived from biorenewable resources that have sufficient volumetric energy densities (enthalpies of reaction per unit volume) and combustion characteristics to make them suitable for transportation applications. Generally, transportation fuels are confined to liquids including hydrocarbons, alcohols, and esters that are readily vaporized and burned within heat engines.

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Hydrogen may eventually be classified as a practical transportation fuel if gas storage technologies can substantially improve over present storage methods based on metal hydrides and high-pressure tanks. Wood and other solid biomass, despite respectable energy densities, do not have handling and combustion characteristics suitable for transportation fuels. The literature often fails to distinguish between *fuels*, which are any substances that can be burned for the production of heat or power, and *transportation fuels*, which is a distinct subset of fuels. The distinction is important because of the more exacting specifications required for transportation fuels.

Chemicals usually are taken to be commodity chemicals, such as acetic acid and propylene glycol, although it can include fine chemicals such as proteins and pharmaceutical chemicals. Commodity chemicals find applications in the manufacture of a wide variety of products including absorbents, adhesives, solvents, lubricants, inks, pesticides, coatings, films, and polymers. Some chemicals, such as ethanol, can be classified as either chemical or transportation fuel, depending upon its ultimate application.

Natural fibers are the elongated cells in the tissues of vascular plants that serve a structural function. Very long, fine fibers such as cotton are used in the manufacture of cloth, while wood fiber is the source of pulp in papermaking. Clearly, polymers synthesized from biorenewable resources can be spun into fibers, but these are synthetic fibers. In this book, fibers separated from biorenewable resources are classified as natural fibers, whereas fibers spun from polymers that have been synthesized from biorenewable resources are classified as synthetic fibers.

The following sections describe the application and potential markets for products from biorenewable resources. In the case of process heat and biopower, this involves a description of the equipment used to convert thermal energy or gaseous fuel generated from biomass into heat and power. The section on biofuels describes issues related to the satisfactory use of liquid fuels derived from biorenewable resources in transportation applications. The section on chemicals will introduce the reader to commodity chemicals in today's markets and indicate where chemicals from biorenewable resources might find market entry. Finally, the section on fibers will explain how natural fibers, once separated from plant materials, can be manipulated into biobased products.

6.2 Process Heat

Oxidation of carbon–carbon and carbon–hydrogen bonds in carbohydrates, lipids, and protein are exothermic reactions. Thus, sufficiently dried, any biorenewable resource can be burned as a source of thermal energy. In practice, sugars, starches, lipids, and proteins are too valuable in the production of food, transportation fuels, and chemicals to be burned for heat or even power. Only lignocellulosic materials,

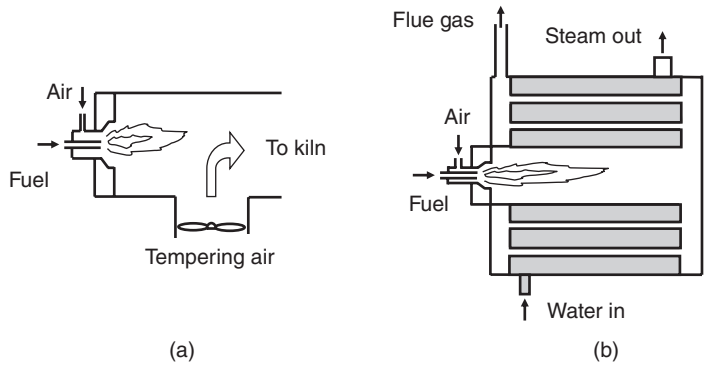


FIG. 6.1 Examples of process heaters: (a) direct-fired burner for a kiln; (b) indirect-fired water-tube boiler.

such as wood and straw, and mixed waste streams, like manure or municipal solid wastes, are likely candidates for process heat, either by directly burning them as solid fuel or after processing them to flammable gases or liquids (see Chapter 8).

Process heat may be required at temperatures as low as 30°C, for example, in heating an anaerobic digester, or as high as 2500°C, for example, in calcining limestone for the production of concrete. Fired process equipment, also known as a *furnace*, is used to burn fuel and deliver process heat at a desired temperature. As illustrated in Figure 6.1, process heaters can be either directly fired or indirectly fired.

6.2.1 Direct-Fired Furnaces

Direct-fired furnaces either burn fuel directly in the process stream or the flue gas from combustion is brought into contact with the process stream. The most common examples of direct-fired furnaces are grain driers, wood kilns, cement kilns, and metal forging ovens. As illustrated in Figure 6.1a, temperature control is achieved by adding air in excess of what is required to burn the fuel. Direct firing has the disadvantage of potentially introducing contaminants from the flue gas stream into the process stream. Although flue gas from the combustion of biomass is primarily a mixture of nitrogen, carbon dioxide, water vapor, and lesser amounts of oxygen, it also contains traces of alkali metals (sodium and potassium), acid gases (hydrogen chloride, sulfur dioxide, and nitrogen oxides), and tar, which is a mixture of oxygenated organic compounds. Modern standards of quality control preclude direct-fired furnaces fueled by biomass except in a few circumstances, such as wood drying or calcining of limestone. On the other hand, if the biomass is first converted to flammable gases, by either thermal gasification or anaerobic digestion, followed by a gas-cleaning step, the resulting gases may be suitable for

use in direct-fired furnaces. However, gas cleaning results in additional capital cost. This cleaning step may be justified for advanced power generation, as subsequently described, but may not be economical for process heat applications.

6.2.2 Indirect-Fired Furnaces

Indirect-fired furnaces do not allow the products of combustion to come in direct contact with the process stream. When very high temperature process heat is required, the combustion stream is separated from the process stream by a thermally conducting wall. Such *process heaters* are commonly used for cracking hydrocarbons or as reboilers in distillation of heavy petroleum liquids.

Another approach to indirect-fired furnaces is to employ a heat-transfer media to move thermal energy from the combustion stream to the process stream. *Air-to-air heat exchangers* have been successfully used in conjunction with biomass combustors to transfer heat from hot, dirty flue gas to a clean air stream. The relatively low convection coefficients associated with gas, however, result in large heat exchangers. *Thermal fluid heaters* are employed in applications where high-pressure steam is to be avoided as heat transfer media. Suitable thermal fluids include water for relatively low temperature applications (100–250°C) and low vapor pressure organic liquids for moderate temperature applications (250–400°C). *Boilers* use steam as a clean, non-corrosive, high-energy content heat transfer media capable of operating at moderately high temperatures (200–540°C). The steam generated is suitable for either direct-contact or indirect-contact heat exchange with process streams.

A *fire-tube boiler*, illustrated in Figure 6.1b, consists of a large, cylindrical shell containing water to be converted to steam. Through the center of this vessel passes a large diameter "fire tube" where combustion of the fuel occurs. The flue gas produced exits through a bundle of smaller tubes surrounding the central fire tube. These boilers are most suited for gaseous or volatile liquid fuels. *Water-tube boilers* consist of a large chamber or firebox that is either penetrated or surrounded by small-diameter tubes containing water. Fuel is burned in the firebox at high temperatures with heat transmitted to the steam tubes by radiation from the flame and by convection from the hot flue gases. Water-tube boilers are the most appropriate technology for direct combustion of biomass fuels. Raising steam from biomass fuels is examined in Chapter 8.

6.3 Biopower

A variety of thermodynamic cycles have been devised to convert heat into work. Power cycles of relevance to biopower include the Stirling, Otto, Diesel, Rankine, and Brayton cycles. From a theoretical perspective, the thermodynamic efficiencies

of all five of these cycles are limited by the Carnot efficiency, which states that the maximum efficiency η_{max} of a heat engine is a function of the temperatures at which the engine receives heat from a high temperature T_H and rejects heat to a low temperature T_L.

$$\eta_{max} = 1 - \frac{T_L}{T_H} \tag{6.1}$$

Accordingly, heat engines must operate at temperatures as high as can be tolerated by the materials of construction in order to achieve the maximum conversion of chemical energy into work. This limit, along with various irreversibilities such as friction, turbulence, and heat transfer, restricts thermodynamic efficiencies of practical heat engines to the range of 35–50%.

6.3.1 Stirling Cycle

The Stirling cycle is an example of an external combustion engine; that is, the products of combustion do not come into contact with the fluid that undergoes the thermodynamic processes of the cycle. In this respect, it resembles the Rankine steam cycle although its thermodynamic efficiency is theoretically higher than that of the Rankine cycle operating on the same fuel. In practice, the efficiencies of Stirling engines are relatively modest as are their output power, typically no more than a few kilowatts. They continue to attract attention mainly because of their low maintenance, high tolerance to contaminants, and relatively low pollution emissions. However, high costs have prevented significant market entry.

6.3.2 Otto and Diesel Cycles

Internal combustion engines are the practical manifestations of the Otto and Diesel cycles. They are robust in operation, efficient at small scales, and are more tolerant of contaminants than are gas turbines. Nevertheless, they are generally confined to niche markets for stationary power applications. Probably, the most important reason for this situation is a limit on their size, which is on the order of 5 MW. Economies of scale, which indicates that the cost of a product goes down as the production facility gets larger, has led the electric utility industry to build power plants that typically produce hundreds if not thousands of megawatts of electricity. Internal combustion engines cannot compete in this arena. Even at the scale of hundreds of kilowatts, internal combustion engines may not be attractive for future biopower applications because of their relatively high pollution emissions and limited opportunities to enhance their efficiency. Application of internal combustion engines for vehicular propulsion is discussed in the section on transportation fuels.

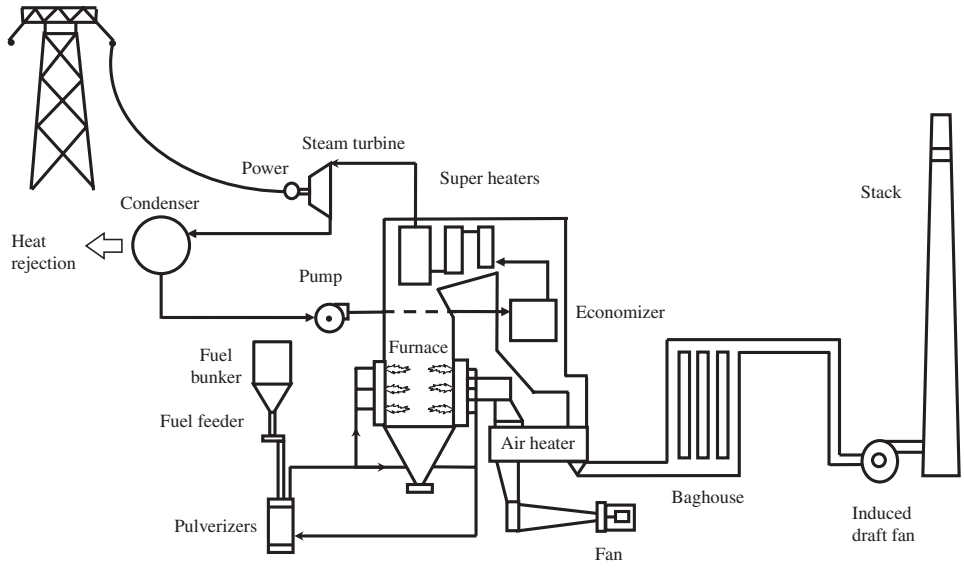


FIG. 6.2 Rankine steam power plant.

6.3.3 Rankine Cycle

The Rankine cycle is another example of an external combustion cycle. As illustrated in Figure 6.2, fuel is burned in a furnace where the released heat is transferred to pressurized water contained within steel tubes. Steam generated in this process is expanded in a steam turbine, which drives an electric generator to produce electric power. The steam is condensed in a water-cooled condenser, which controls the temperature exiting the turbine and thus sets T_L in Equation 6.1.

The Rankine steam power cycle has been the foundation of stationary power generation for over a century. Although Brayton cycles employing gas turbines and electrochemical cycles based on fuel cells will constitute much of the growth in power generation in the future, steam power plants will continue to supply the majority of electric power for decades to come and will find new applications in combination with advanced generation technologies. The reason for the Rankine cycle's preeminence has been its ability to directly fire coal and other inexpensive fuels. Constructed at scales of several hundred megawatts, the modern steam power plant can convert as much as 45% of chemical energy in fuel to electricity at a cost of $0.02–$0.05 per kilowatt.

Utility-scale steam power plants are not expected to dominate future growth in electric power infrastructure in the United States. These giant plants take several years to plan and construct, which decreases their financial attractiveness in increasingly deregulated power markets. Coal and other fossil fuels burned

in these plants are major sources of air pollution, including sulfur and nitrogen oxides, both of which are precursors to acid rain and the latter an important factor in smog formation; fine particulate matter, which is implicated in respiratory disease in urban areas; and heavy metals, the most prominent being mercury, which accumulates in the biosphere to toxic levels. Substitution of biorenewable resources such as wood and agricultural residues for coal in existing power plants could substantially reduce pollution emissions, although these plants are so large that the locally available biomass resources could supplant only a small fraction of the total energy requirement. Small-scale steam power plants sized for use of local biomass resources have low thermodynamic efficiencies, on the order of 25%, making them wasteful of energy resources.

6.3.4 Brayton Cycle

The Brayton cycle produces electric power by expanding hot gas through a turbine. These gas turbines operate at temperatures approaching 1300°C compared to inlet temperatures of less than 650°C for steam turbines used in Rankine cycles. Although this difference in inlet temperature (T_H in Equation 6.1) would suggest that Brayton cycles have much higher thermodynamic efficiencies than Rankine cycles, the Brayton cycle also has much higher exhaust temperature (T_L in Equation 6.1) than does the Rankine cycle. Gas turbine exhaust temperatures are in the range of 400–600°C, whereas steam turbine exhaust temperatures are on the order of 20°C. Furthermore, Brayton cycles, which contain both a gas compressor and gas turbine, have more sources of mechanical irreversibilities, further degrading thermodynamic efficiencies, which may only be marginally higher than the best Rankine steam cycles. However, improvements in gas turbine technology that allow operation at higher temperatures and pressures are expected to increase Brayton cycle efficiency for large power plants to greater than 50%, although 30% is more realistic for gas turbines sized appropriately for biomass power plants.

The two general classes of gas turbines for power generation are heavy-duty industrial turbines and lightweight aeroderivative gas turbines. The aeroderivatives are gas turbines originally developed for commercial aviation but adapted for stationary electric power generation. They are attractive for biopower applications because of their high efficiency and low unit capital costs at the modest scales required for biomass fuels.

Gas turbines are well suited to gaseous and liquid fuels, which are relatively free of contaminants that rapidly erode or corrode turbine blades. In this respect, gas turbine engines are not suitable for directly firing most biomass fuels. Solid biomass releases significant quantities of alkali metals, chlorine, mineral matter, and lesser amounts of sulfur upon burning. These would be entrained in the gas flow entering the expansion turbine where they would quickly contribute to blade failure. Cleaning large quantities of hot flue gas is not generally considered an

economical proposition. Even the gas released from anaerobic digestion contains too much hydrogen sulfide to be directly burned in a gas turbine without first chemically scrubbing the gas to remove this corrosive agent.

Nevertheless, gas turbine engines are considered one of the most promising technologies for biopower because of the relative ease of plant construction, cost-effectiveness in a wide range of sizes (from tens of kilowatts to hundreds of megawatts), and the potential for very high thermodynamic efficiencies when employed in advanced cycles. The key to their success in biopower applications is converting the biomass to clean-burning gas or liquid before burning it in the gas turbine combustor. Chapter 8 explores technologies suitable for this purpose.

6.3.5 Combined Cycles

In an effort to enhance energy conversion efficiency, combined cycle power systems have been developed, which recognize that waste heat from one power cycle can be used to drive a second power cycle. Combined cycles would be unnecessary if a single heat engine could be built to operate between the temperature extremes of burning fuel (T_H) and the ambient environment (T_L). However, temperature and pressure limitations on materials of construction have prevented this realization. Combined cycles employ a topping cycle designed to operate between T_H and some intermediate temperature T_I and a bottoming cycle designed to operate between T_I and T_L. The overall efficiency of a combined cycle power system is

$$\eta_C = \eta_T + \eta_B - \eta_T \eta_B \tag{6.2}$$

where η_C, η_T, and η_B are the efficiencies of the combined cycle, topping cycle, and bottoming cycle, respectively. Most commonly, combined cycle power plants employ a gas turbine engine for the topping cycle and a steam turbine plant for the bottoming cycle, achieving overall efficiencies of 60% or higher.

Clean-burning fuel from biomass for use in a combined cycle can be obtained by thermal gasification or anaerobic digestion to produce gas or by fast pyrolysis to produce liquid. Integrated gasification/combined cycle (IGCC) power is illustrated in Figure 6.3. Compressed air enters an oxygen plant, which separates oxygen from the air. The oxygen is used to gasify biomass in a pressurized gasifier to produce medium heating-value producer gas. The producer gas passes through cyclones and a gas clean-up system to remove particulate matter, tar, and other contaminants that may adversely affect gas turbine performance (alkali and chloride being the most prominent among these). These clean-up operations are best performed at high temperature and pressure to achieve high cycle efficiency. The clean gas is then burned in air and expanded through a gas turbine operating as a "topping" cycle. The gas exits the turbine at temperatures ranging between 400°C and 600°C. A heat recovery steam generator produces steam for a "bottoming" cycle that employs

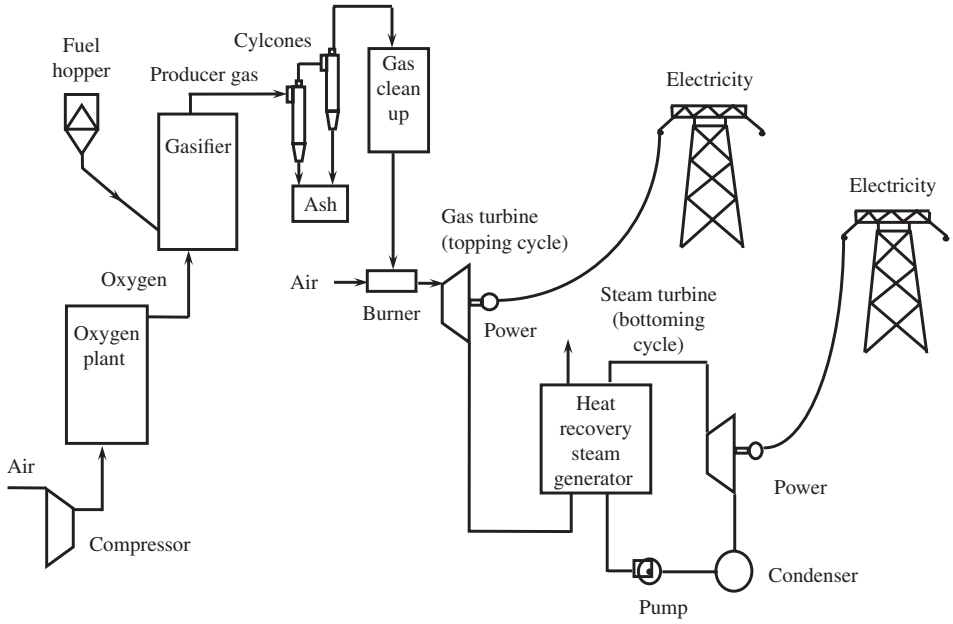


FIG. 6.3 Integrated gasification/combined cycle power plant based on a gas turbine topping cycle.

a steam turbine. Electric power is produced at two locations in this plant, yielding thermodynamic efficiencies exceeding 47%.

IGCC systems based on gas turbines are attractive for several reasons. These reasons include their relative commercial readiness and the expectation that they can generate electricity at the lowest cost of all possible biomass power options.

An alternative to IGCC is to generate steam for injection into the gas turbine combustor, which increases mass flow and power output from the turbine. This variation, called a steam-injected gas turbine (STIG) cycle, is less capital intensive than IGCC, since it does not employ a steam turbine. The STIG cycle is commercially developed for natural gas; lower flammability limits for producer gas make steam injection more problematic for biomass-derived producer gas. The intercooled steam-injected gas turbine (ISTIG) is an advanced version of the STIG. This cycle further improves thermodynamic efficiency by cooling gas flow between several stages of compression (intercooling).

6.3.6 Fuels Cells

Among the most exciting new energy technologies are fuel cells, which directly convert chemical energy into work, thus bypassing the restriction on efficiency imposed by the Carnot relationship. This does not imply that fuel cells can convert

100% of chemical enthalpy of a fuel into work, as the process still must conform to the laws of thermodynamics. Thermodynamic efficiency, as defined in Chapter 2, is the ratio of useful energy out to the total energy into the process. For a fuel cell, the useful energy out is the electrical work generated. From thermodynamics, it is known that the maximum theoretical work for a chemical reaction is equal to the change in Gibbs function ΔG for the reaction. The total chemical energy entering the fuel cell is the enthalpy of reaction ΔH. Therefore, the maximum efficiency of a fuel cell operating at 1 atm of pressure is

$$\eta_{\max} = \frac{E_{\text{out}}}{E_{\text{in}}} = \frac{\Delta G^{\circ}}{\Delta H^{\circ}} = \frac{\Delta H^{\circ} - T\Delta S^{\circ}}{\Delta H^{\circ}} = 1 - T\frac{\Delta S^{\circ}}{\Delta H^{\circ}} \tag{6.3}$$

where the superscript indicates calculation at 1 atm of pressure. All practical fuel cells to date are based on the oxidation of hydrogen:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \tag{6.4}$$

which has an enthalpy of reaction of –285 830 kJ/kmol and entropy of reaction of −163 kJ/kmol-K at 25°C. Thus, a fuel cell operating at 25°C (298 K) has a theoretical maximum efficiency of

$$\eta_{\max} = \left[1 - 298\text{K}\frac{(-163\text{ kJ/kmol-K})}{(-285\,830\text{ kJ/kmol})}\right] \times 100 = 83\% \tag{6.5}$$

Irreversibilities acting on the fuel cell reduce this efficiency to 35–60%, depending upon the fuel cell design. Thus, fuel cells can produce significantly more work from a given amount of fuel than can heat engines. However, carbonaceous fuels must first be reformed to hydrogen before they are suitable for use in fuel cells. The energy loses associated with fuel reforming must be included when determining the overall fuel-to-electricity conversion efficiency of a fuel cell.

The operation of a fuel cell is illustrated schematically in Figure 6.4. The device consists of two gas-permeable electrodes separated by an electrolyte, which is a transport medium for electrically charged ions. Hydrogen gas, the ultimate fuel in all current designs of fuel cells, enters the fuel cell through the anode, while oxygen is admitted through the cathode.

Depending on the fuel cell design, either positively charged hydrogen ions form at the anode or negatively charged ions containing oxygen form at the cathode. In either case, the resulting ions migrate through the electrolyte to the opposite electrode from which they are formed. Hydrogen ions migrate to the cathode where they react with oxygen to form water. Oxygen-bearing ions migrate to the anode where they react with hydrogen to form water. Both ionic processes release chemical

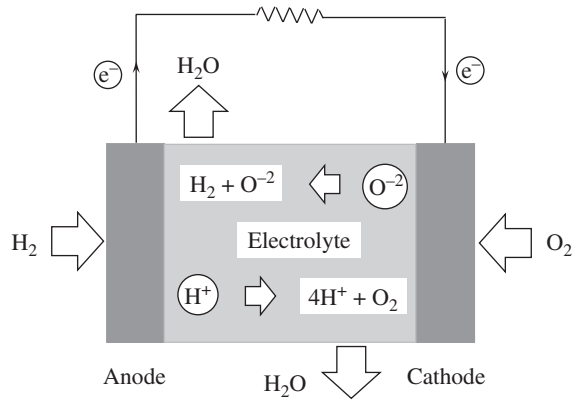


FIG. 6.4 Schematic of operation of fuel cell.

energy in the form of electrons at the anode, which flow to the cathode through an external electric circuit. This external flow of electrons represents the direct generation of electric power from flameless oxidation of fuel. The inherently high thermodynamic efficiency of fuel cells makes them attractive for biomass power where fuel costs are relatively expensive compared to many fossil fuels.

Several types of fuel cells have been developed, which are classified according to the kind of electrolyte employed: phosphoric acid, polymeric, molten carbonate, and solid oxide. Despite differences in materials and operating conditions, all are based on the electrochemical reaction of hydrogen and oxygen. For integrated gasification/fuel cell power systems, the molten carbonate and solid oxide systems are of particular interest because of their high-temperature operation, which allows waste heat recovery and use in advanced power cycles.

The first generation of fuels cells employs phosphoric acid as the electrolyte. Operated at 200°C, it attains efficiencies of 35–45%. Although well developed, commercial application has been limited by its use of expensive platinum catalysts, which are deactivated by CO.

Proton exchange membrane fuel cells were originally developed for space applications but are also considered attractive for automotive propulsion. The electrolyte is a solid polymeric material operated at less than 100°C; both factors contribute to the ease of construction and operation of this fuel cell. Efficiencies range between 35% and 60%. However, this fuel cell is intolerant of CO, which can be difficult to exclude from on-board reformed fuels. It would also require the use of "cold" gas, which reduces the efficiency of a gasification-based power system.

The molten carbonate fuel cell operates at about 650°C. Although hydrogen is the ultimate energy carrier, this fuel cell can be operated on a variety of hydrogen-rich fuels, including methane, kerosene, diesel fuel, ethanol, and producer gas. Within the fuel cell, a reformer converts these fuels into mixtures of hydrogen,

carbon monoxide, carbon dioxide, and water along with varying amounts of unreformed fuel. Overall efficiency of converting methane into electricity is 45–55%. Molten carbonate fuel cells have completed extensive demonstration trials, but they have unresolved materials problems related to the use of corrosive alkali carbonate as electrolyte.

The solid oxide system is also a high-temperature fuel cell, operating at 650–1000°C. The electrolyte is a porous ceramic material, usually based upon yttrium and zirconium. The solid electrolyte provides for a simpler, less expensive design and longer expected life than other fuel cell systems. Efficiencies are between 50% and 60%. The higher operating temperature compared to the molten carbonate system also enhances its attractiveness for heat recovery and use in advanced power systems. Most solid oxide fuel cells operate with a steam reformer in which water vapor and carbon monoxide react according to the water–gas shift reaction to produce hydrogen, thus making them compatible with carbon monoxide-rich producer gas as fuel. Solid oxide systems may solve some of the corrosion problems associated with molten carbonate fuel cells.

The gas mixture produced by a biomass gasifier contains dust and tar that must be removed or greatly reduced for most applications, including power generation in fuel cells. Removal of tar would ideally be performed at elevated temperatures. If the gas is to be used in fuel cells, further cleaning is required to remove ammonia (NH_3), hydrogen chloride (HCl), and hydrogen sulfide (H_2S). Table 6.1 details contaminant removal requirements for various kinds of fuel cells. To obtain high energy efficiency, trace contaminant removal must be performed at elevated temperatures for fuel cells that operate at relatively high temperatures. Low-temperature fuel cells cannot tolerate CO, which can be removed by the water–gas shift reaction. The catalysts that facilitate the shift reaction, however, are poisoned by trace contaminants, which must be removed prior to the shift reactors. One method for removing H_2S and HCl is the use of a fixed bed of calcined dolomite or limestone and zinc titanate at temperatures around 630°C. This is followed by steam reforming at high temperature (750–850°C) to destroy tar and ammonia.

Table 6.1 Contaminants for various fuel cell systems

		Contaminant Tolerance Level			
Fuel Cell Type	Classification	H_2S	HCl	NH_3	CO
Solid polymer	Low temperature	–	–	–	10 ppm
Phosphoric acid	Low temperature	50 ppm	–	–	5%
Molten carbonate	High temperature	0.5 ppm	10 ppm	1%	–
Solid oxide	High temperature	0.1 ppm	1.0 ppm	0.5%	–

Source: US Department of Energy National Energy Technology Laboratory (2000) *Fuel Cell Handbook*, 5th edn. CD-ROM. Morgantown, WV/Pittsburgh, PA: US Department of Energy National Energy Technology Laboratory.

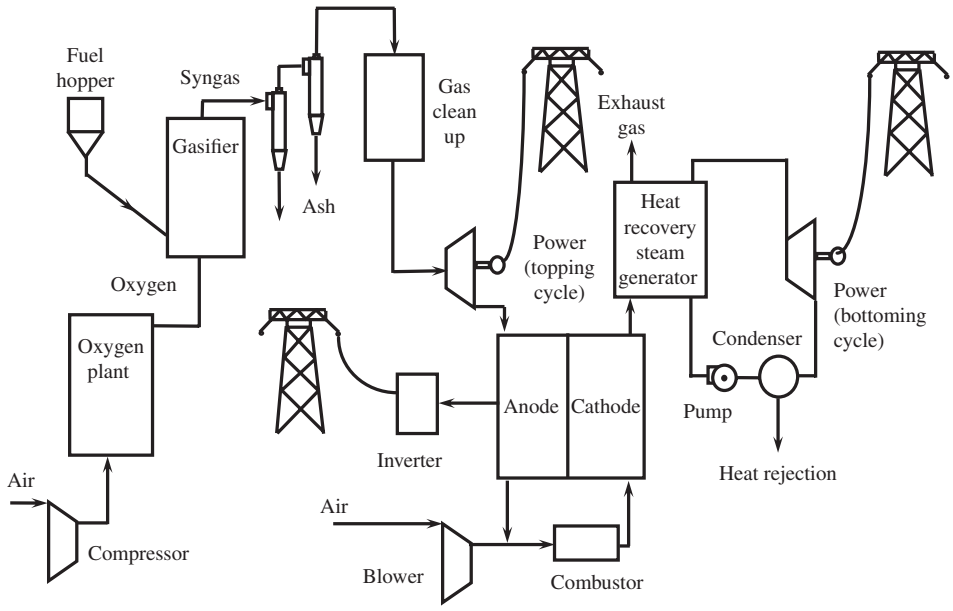


FIG. 6.5 Combined cycle power plant based on high-temperature fuel cells.

Figure 6.5 illustrates an IGCC power plant based on a molten carbonate fuel cell. Biomass is gasified in oxygen to yield producer gas. Gasification occurs at elevated pressure to improve the yield of methane, which is important for proper thermal balance of this fuel cell. Hot-gas clean up to remove particulate matter, tar, and other contaminants is followed by expansion through a gas turbine as part of a topping power cycle. The pressure and temperature of the producer gas is sufficiently reduced after this to admit it into the fuel cell. High-temperature exhaust gas exiting the cathode of the fuel cell enters a heat recovery steam generator, which is a part of a bottoming cycle in the integrated plant. Thus, electricity is generated at three locations in the plant for an overall thermodynamic efficiency reaching 60% or more.

6.4 Biofuels

Almost 25% of energy consumption in the United States is consumed by transportation needs. Approximately 40% of this amount comes from imported petroleum. Thus, development of transportation fuels from biorenewable resources is a priority if decreased dependence on foreign sources of energy is to be achieved.

Traditional transportation fuels exploit the different boiling points of hydrocarbons that make up petroleum (see Figure 6.6). Boiling point increases as the

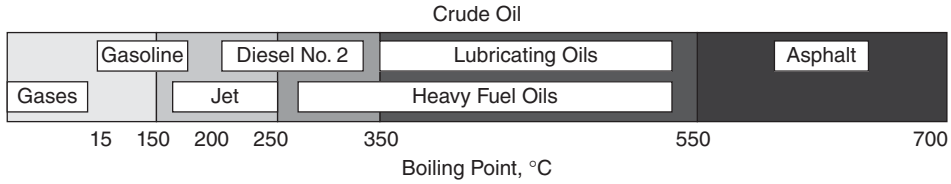


FIG. 6.6 Conventional transportation fuels exploit the wide range of boiling points of petroleum hydrocarbons (note that the high molecular weights of high-boiling-point hydrocarbons can be cracked to smaller molecules).

molecular weight of hydrocarbons increases. Large hydrocarbon molecules can be cracked to smaller molecules with lower boiling points that are suitable as fuels although this requires the additional expenditure of energy and equipment.

The hydrocarbons making up traditional transportation fuels include chains of single-bonded carbon atoms known as straight-chain alkanes or paraffins, branched-chain alkanes known as isoparaffins, rings of single-bonded carbon atoms known as cycloalkanes (sometimes referred to as naphthenes), and six-member rings of carbon with alternating single and double bonds known as aromatics. For example, as illustrated in Figure 6.7, gasoline contains C_6 molecules in one of several forms including straight-chain hexane (*n*-hexane), a branched-chain hexane (isohexane), a saturated ring (cyclohexane), or an aromatic ring (benzene). Traditional transportation fuels are classified as gasoline, diesel fuel, or jet fuel.

Gasoline is intended for spark-ignition (Otto cycle) engines; thus, it is relatively volatile but resistant to autoignition during compression. Diesel fuel is intended for use in compression-ignition (Diesel cycle) engines; thus, it is less volatile compared to gasoline and more susceptible to autoignition during compression. Jet fuel is designed for use in gas turbine (Brayton cycle) engines, which are not limited by autoignition characteristics but otherwise have very strict fuel specifications for reasons of safety and engine durability. Gasoline is a mixture of hundreds of

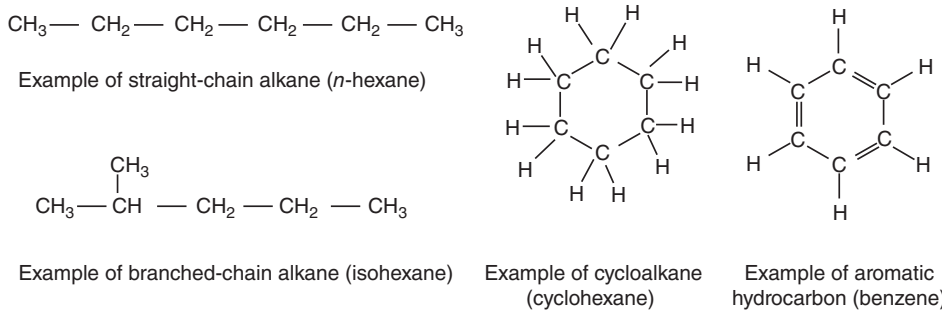

CH3— CH2— CH2— CH2— CH2— CH3
Example of straight-chain alkane (n-hexane)
CH3
CH3— CH — CH2— CH2— CH3
Example of branched-chain alkane (isohexane)
Example of cycloalkane (cyclohexane)
Example of aromatic hydrocarbon (benzene)

FIG. 6.7 Examples of six-carbon atom hydrocarbon molecules found in petroleum-derived transportation fuels.

different hydrocarbons obtained from a large number of refinery process streams that contain between 4 and 12 carbon atoms with boiling points in the range of 25–225°C. Most of the mixture consists of alkanes with butanes and pentanes added to meet vapor pressure specifications. A few percent of aromatic compounds are added to increase octane number, the figure of merit used to indicate the tendency of a fuel to undergo premature detonation within the combustion cylinder of an internal combustion engine. The higher the octane number, the less likely a fuel will detonate until exposed to an ignition source (electrical spark). Premature denotation is responsible for the phenomenon known as engine knock, which reduces fuel economy and can damage an engine. Various systems of octane rating have been developed, including research octane and motor octane numbers. Federal regulation in the United States requires gasoline sold commercially to be rated using an average of the research and motor octane numbers. Gasoline rated as "regular" has a commercial octane number of about 87 while premium grade is 93.

Diesel fuel, like gasoline, is also a mixture of light distillate hydrocarbons but with lower volatility and higher viscosity. Because diesel fuel is intended to be ignited by compression rather than by a spark, its autoignition temperature is lower than for gasoline. The combustion behavior of diesel fuels is conveniently rated according to cetane number, an indication of how long it takes a fuel to ignite (ignition delay) after it has been injected under pressure into a diesel engine. A high cetane number indicates short ignition delay; for example, No. 2 diesel fuel has cetane number of 37–56, while gasoline has a cetane number less than 15.

Jet fuel is designated as either kerosene type (including Jet A, Jet A1, and JP8) or wide cut type (including Jet B and JP4). Kerosene type is a mixture of straight-chain alkane (paraffin) molecules containing 9–20 carbon atoms giving it a relatively high boiling range of 165–290°C, making it similar to diesel fuel. It also contains a certain percentage of aromatic compounds to meet desired fuel performance characteristics. Wide-cut-type jet fuel is a blend of kerosene and gasoline containing 5–15 carbon atoms, which gives it a wider boiling point range. It contains straight-chain and branched-chain alkane molecules as well as aromatic hydrocarbons. Although its lower boiling point range enhances cold-weather performance, it also makes it more flammable and dangerous to handle. At one time it was preferred in the United States because of the wide availability of gasoline for blending with more scarce kerosene. However, safety and environmental concerns have resulted in the phase out of wide-cut-type blends for both commercial and military aviation except in demanding applications.

The primary candidates for liquid biofuels are methanol, ethanol, butanol, biodiesel, and biomass-derived hydrocarbons. Methanol, ethanol, and butanol, by virtue of their high octane numbers, are suitable for use in spark-ignition engines. The high cetane numbers of biodiesel, which are methyl or ethyl esters formulated from vegetable or animal fats, make them suitable for use in compression-ignition engines. Biomass-derived hydrocarbons, depending upon their composition, can

Table 6.2 Comparison of transportation fuels

	Gasoline Hydrocarbons	No. 2 Diesel Fuel Hydrocarbons	Methanol, CH_3OH	Ethanol, C_2H_5OH	Butanol, C_4H_9OH	Biodiesel, Methyl Ester
Specific gravity at 16°C	0.72–0.78	0.85	0.796	0.794	0.81	0.886
Kinematic viscosity at 20°C (m/s)	0.8×10^{-6}	2.5×10^{-6}	0.75×10^{-6}	1.4×10^{-6}	3.2×10^{-6}	3.9×10^{-6}
Boiling point range[a] (°C)	30–225	210–235	65	78	118	315–350
Flash point (°C)	−43	52	11	13	35	100–170
Autoignition temperature (°C)	370	254	464	423	343	–
Octane no. (research)	91–100	–	106	107	96	–
Octane no. (motor)	82–92	–	92	89	78	–
Cetane no.	<15	37–56	<15	<15		55
Heat of vaporization (kJ/kg)	380	375	1185	920	430	–
Lower heating value (MJ/kg)	43.5	45	20.1	27	35.4	37
Vapor pressure (psi at 100F)	4.5	–	4.6	2	0.33	–

Source: Borman, G.L. and Ragland, K.W. (1998) *Combustion Engineering*. McGraw-Hill.[a]Seasonally adjusted for cold and hot weather operation.

be used as direct substitutes for gasoline, diesel, and jet fuel. Properties of these fuels are compared in Table 6.2.

6.4.1 Methanol

In the 1980s, production of methanol from coal was touted as an alternative to petroleum-based fuels. The same process of gasification and fuel synthesis can be used to produce methanol from biomass. Methanol as fuel is characterized by narrow boiling point range, high heat of vaporization, and high octane number. It has only 49% of the volumetric heating value of gasoline. As fuel, methanol has many of the same advantages and disadvantages as ethanol but has not met the same acceptance as ethanol for two reasons. First, although biomass-to-methanol is economically attractive compared to many alternative routes to biofuels, the capital investment for gasification and catalytic synthesis equipment is very high. In contrast, ethanol can be fermented from sugar or starch crops for relatively modest capital investment. Second, methanol is considerably more toxic than ethanol. The closely related and similarly toxic methyl tertiary butyl ether (MTBE) has been banned as fuel oxygenate and octane enhancer because of concerns about ground water contamination. Thus, it seems unlikely that methanol will ever be a serious contender as biofuel. On the other hand, as described in Chapter 8, methanol can be converted to gasoline, which is a more attractive route for transportation fuel from biomass.

6.4.2 Ethanol

Ethanol can be produced by the fermentation of sugar or starch crops. A fuel ethanol market has been developed in Brazil based on sugarcane, while the United States has relied on cornstarch for commercial production of fuel ethanol. Technologies are also being developed to convert lignocellulose into sugars or syngas, a mixture of carbon monoxide and hydrogen, either of which can be fermented into ethanol.

On a volumetric basis, ethanol has only 66% of the heating value of gasoline. Thus, the range of a vehicle operating on pure ethanol is theoretically reduced by a corresponding amount and, accordingly, meaningful comparisons of the cost of gasoline and ethanol should be made on the basis of energy delivered ($/GJ) instead of fuel volume ($/L). However, fuel economy depends on many complex interactions between a fuel and the combustion environment within an engine, which some argue improves the relative performance of ethanol. For example, as Table 6.2 illustrates, ethanol has a higher latent heat of vaporization compared to gasoline. This promotes cooler operation of the engine, allowing higher densities of fuel and air to be burned in the engine. Furthermore, ethanol, with molecular formula of C_2H_5OH, has a much lower stoichiometric air–fuel ratio than gasoline, nominally taken to have the molecular formula of octane (C_8H_{18}); thus a higher energy density can be achieved in the engine. These factors result in higher inducted fuel energy densities, which can produce both higher power outputs and improved engine efficiency compared to gasoline-fueled vehicles. Finally, the higher octane number for ethanol compared to gasoline (109 vs. 91–101) allows engines to be designed to run at higher compression ratios, which improves both power and fuel economies. Estimates for efficiency improvements in engines optimized for ethanol instead of gasoline range from 15% to 30%, resulting in a driving range approaching 80% of that of gasoline.

Internal combustion engines can be fueled on pure ethanol (known as neat alcohol or E100) or blends of ethanol and gasoline. Brazil employs 190 proof ethanol (95 vol% alcohol and 5% water), which eliminates the energy-consuming step of producing anhydrous ethanol. In the United States two ethanol–gasoline blends are common: E85 contains 85% ethanol and 15% gasoline and E10, at one tme referred to as gasohol, contains only 10% ethanol with the balance being gasoline. The advantage of E10 is that it can be used in vehicles with engines designed for gasoline; however, its use is accompanied by a loss in fuel economy (as measured in km/L or miles/gal) compared to gasoline, amounting to 2–5%.

A significant problem with ethanol–gasoline blends is water-induced phase separation. Water contaminating a storage tank or pipeline is readily absorbed by ethanol, resulting in a lower water-rich layer and an upper hydrocarbon-rich layer, which interferes with proper engine operation. Water contamination is a problem that has not been fully addressed by the refining, blending, and distribution

industries; thus, transportation of ethanol–gasoline blends in pipelines is not permitted in the United States and long-term storage is to be avoided.

6.4.3 Butanol

Butanol (C_4H_9OH), by virtue of its longer carbon chain length, is less soluble in water and has higher heating value than methanol and ethanol. For this reason, butanol has some attraction as motor fuel. Its energy content is within 10% of gasoline and its octane number, although lower than ethanol, is greater than gasoline's. Its low vapor pressure is attractive in reducing volatile organic matter emissions, but it can make cold starting more difficult. Butanol is only moderately soluble in water, an important advantage compared to fully soluble methanol and ethanol. Although not currently used as transportation fuel, very likely butanol would be substituted for ethanol if its fermentation from sugar or starch crops became economically feasible.

6.4.4 Biodiesel

Vegetable oils, which are triglycerides of fatty acids, have long been recognized as potential fuels in diesel engines. Compared to petroleum-based diesel fuels, vegetable oils have higher viscosity and lower volatility, which result in fouling of engine valves and less favorable combustion performance, especially in direct-injection engines. The solution to this problem is to convert the triglycerides into methyl esters or ethyl esters of the fatty acids, known as biodiesel, and the byproduct 1,2,3-propanetriol (glycerol).

Table 6.2 illustrates that fuel properties of biodiesel are very similar to petroleum-based diesel. The specific gravity and viscosity of biodiesel are only slightly higher than for diesel, while the cetane numbers and heating values are comparable. Significantly higher flash points for biodiesel represent greater safety in storage and transportation. Biodiesel can be used in unmodified diesel engines with no excess wear or operational problems. Tests in light and heavy trucks showed few differences other than a requirement for more frequent oil changes because of the buildup of ester fuel in engine crankcases.

6.5 Chemicals

Chemicals are the broadest class of biobased products. It would be impossible to describe all possible chemical products from biorenewable resources in this section. Instead, an effort is made to focus on potential commodity chemicals from biorenewable resources although fine chemicals and pharmaceuticals are also potential products. Table 6.3 lists the top 60 commodity chemicals in the United States in terms of their annual production. The feedstock employed and

Table 6.3 Sixty major organic chemicals manufactured in the United States

No.	Product	Annual Production (10^9 kg)	Usual Organic Feedstock	Energy Consumed per Product Mass		Average Market Price ($/kg)
				Process (MJ/kg)	Feed (MJ/kg)	
1.	Ethylene	21.30	Natural gas liquids	23.3	58.1	0.55
2.	Propylene	11.65	Natural gas liquids	16.3	56.8	0.42
3.	MTBE	7.99	C_4H_8/methanol	13.0	50.5	0.29
4.	Ethylene dichloride	7.83	C_2H_4	4.0	42.2	0.37
5.	Benzene	7.24	BTX	2.3	81.2	0.33
6.	Urea	7.07	$CO_2(NH_3)$	2.8	30.6	0.20
7.	Vinyl chloride	6.79	C_2H_4	17.4	53.4	0.45
8.	Ethylbenzene	6.19	C_2H_4/benzene	2.3	66.5	0.56
9.	Styrene	5.16	Ethylbenzene	12.8	74.3	0.64
10.	Methanol, synthetic	5.12	CO/(H_2)	11.6	25.8	0.21
11.	Mixed xylenes	4.25	BTX	10.2	43.0	0.31
12.	Ethanol, fermentation	3.90	Corn	18.8	31.0	0.42
13.	Formaldehyde (37 wt%)	3.68	Methanol	0.0	43.9	0.24
14.	Terephthalic acid	3.61	*p*-Xylene	12.8	57.8	0.88
15.	Ethylene oxide	3.46	C_2H_4	0.4	68.1	0.99
16.	Toluene	3.05	BTX	10.2	43.0	0.31
17.	*p*-Xylene	2.88	BTX	22.3	59.1	0.46
18.	Cumene	2.55	C_3H_6/benzene	2.3	66.2	0.51
19.	Ethylene glycol	2.37	Ethylene oxide	13.9	49.6	0.37
20.	Acetic acid, synthetic	2.12	Methanol/(CO)	10.7	27.7	0.79
21.	Phenol, synthetic	1.89	Cumene	15.1	99.3	0.90
22.	Propylene oxide	1.81	Propylene	16.3	58.4	1.41
23.	1,3-Butadiene	1.67	Butanes/enes	51.1	58.4	0.49
24.	Carbon black	1.51	Residual oil	27.9	93.0	0.64
25.	Isobutylene	1.47	Butanes/enes	9.3	85.3	0.68
26.	Acrylonitrile	1.45	Propylene	6.0	78.8	1.17
27.	Vinyl acetate	1.31	C_2H_4/HOAc	15.6	59.2	0.97
28.	Acetone	1.25	Cumene	15.1	99.3	0.86
29.	Butraldehyde	1.22	Propylene/(CO)			0.95
30.	Cyclohexane	0.969	Benzene	2.3	58.1	0.44
31.	Adipic acid	0.816	Cyclohexane	29.1	84.0	1.62
32.	Nitrobenzene	0.748	Benzene			0.73
33.	Bisphenol A	0.736	Acetone/phenol			2.07
34.	Caprolactam	0.714	Cyclohexanone	7.9	54.5	2.05
35.	Acrylic acid	0.698	Propylene			1.92
34.	Caprolactam	0.714	Cyclohexanone	7.9	54.5	2.05
35.	Acrylic acid	0.698	Propylene			1.92
36.	*n*-Butanol	0.677	Propylene (CO)			1.10
37.	Isopropyl alcohol	0.646	Propylene			0.71
38.	Aniline	0.631	Nitrobenzene			1.08
39.	Methyl methacrylate	0.622	Acetone/(HCN)			1.32
40.	Cyclohexanone	0.501	Phenol			1.61
41.	Methyl chloride	0.483	Methane			0.85
42.	*o*-Xylene	0.465	BTX			0.42
43.	Propylene glycol	0.462	Propylene oxide			1.43
44.	Phthalic anhydride	0.451	Naphthalene			0.84
45.	Acetone cyanohydrin	0.410	Acetone/(HCN)			0.77
46.	Toluene diisocyanates	0.395	Toluene			2.09

(*continued*)

Table 6.3 (*Continued*)

No.	Product	Annual Production (10^9 kg)	Usual Organic Feedstock	Energy Consumed per Product Mass		Average Market Price ($/kg)
				Process (MJ/kg)	Feed (MJ/kg)	
47.	Dodecylbenzene	0.386	C_6H_6/dodecene			1.25
48.	Ethanol amines	0.369	Ethylene oxide			1.26
49.	Diethylene glycol	0.354	Ethylene oxide			0.71
50.	Carbon tetrachloride	0.344	Methane			0.79
51.	2-Ethyl-1-hexanol	0.337	C_3H_6/CO or RCHO			1.23
52.	Ethanol, synthetic	0.284	Ethylene	4.7	31.4	0.42
53.	Isoprene	0.281	HC/turpentines			0.68
54.	1,4-Butanediol	0.266	C_3H_6/CO or THF			1.24
55.	Methyl ethyl ketone	0.264	2-Butanol			1.01
56.	Ligninsulfonic acid salt	0.258	Sulfite liquor			0.36
57.	Chloroform	0.256	Methane			0.87
58.	Maleic anhydride	0.251	Benzene			0.93
59.	C12-benzenesulfonate Na	0.217	C_6H_6/dodecene			1.34
60.	1-Butene	0.209	Ethylene			0.57

Source: Klass, D.L. (1998) *Biomass for Renewable Energy, Fuels, and Chemicals*. San Diego: Academic Press.

the energy consumed in their production as well as their selling prices in 1995 are also listed (prices of commodity chemicals can fluctuate widely, even during the course of a year, so current market reports should be consulted if accurate prices are important).

In principle, all organic compounds can be synthesized from biorenewable resources. In practice, current economics favors chemical synthesis from fossil resources, especially from petroleum and natural gas, except for a few oxygenated organic compounds. The following three sections summarize three categories of potential biobased chemicals: commercially important chemicals that are currently produced from fossil resources but could also be produced from biorenewable resources, those that are currently produced from biorenewable resources, and unexploited chemicals with future potential in the manufacture of biobased products.

6.5.1 Chemicals Produced from Fossil Resources

The petrochemical industry is built on seven basic building blocks: syngas from methane (CH_4), ethylene (ethene—C_2H_4), propylene (propene—C_3H_6), butanes (C_4H_{10}), butylene (butene—C_4H_8), butadiene (C_4H_6), and BTX, the latter of which is a mixture of the closely related compounds benzene, toluene (methylbenzene), and xylene (dimethylbenzene). Methane is obtained from natural gas. Ethylene, propylene, butane, butylene, and butadiene are obtained from natural gas liquids, refinery off-gases, and petroleum. Benzene, toluene, and xylene, the basis for aromatic compounds, are obtained from petroleum and coal. From these

seven building blocks, all the organic compounds of the modern world can be obtained.

The following paragraphs describe several industrially important organic compounds, currently obtained from fossil resources that might be obtained in the future from biorenewable resources.

Ethylene

Ethylene is the leading organic chemical manufactured in the United States and is the starting point for a wide variety of consumer and industrial products including polymers (polyethylene, polystyrene, and polyester) and polyols (ethylene glycol). It is commercially produced from natural gas liquids.

Ethylene can also be produced by dehydration of ethanol in the presence of an acid catalyst. Thus, some have suggested the conversion of inexpensive lignocellulosic biomass into ethanol followed by the manufacture of biobased ethylene. Although Brazil built a commodity chemical industry on this process, the relatively low cost of natural gas makes this an unlikely prospect in other markets for the foreseeable future.

1,3-Butadiene

Sixty percent of 1,3-butadiene (C_4H_6) production in the United States is used to produce elastomers such as styrene/butadiene, polybutadiene, neoprene, and nitrile rubber. The largest single market for butadiene is the manufacture of tires. Smaller amounts go into other consumer and industrial products. Butadiene is manufactured in the petroleum industry by thermal cracking of natural gas liquids.

Pentane/Pentene

Pentane (C_5H_{12}) is used as a solvent, as a blending component of high-octane gasoline, and in processing isoprene. Pentene (C_5H_{10}) is used in the formulation of plasticizers and detergents and is a precursor to the production of thiols, amines, and ammonium salts. Pentenes have been used as monomers for the manufacture of resins and low-molecular-weight thermoplastic materials. Thermal cracking of naphtha and gas oil yields ethylene and propylene as the primary products and five carbon hydrocarbons as byproducts, from which are distilled pentane and pentene.

Benzene

The single largest use of benzene (C_6H_6) in the United States is the production of styrene, which finds application in the production of such polymers as polystyrene, acrylonitrile/butadiene/styrene (ABS), styrene/acrylonitrile resins, and styrene/butadiene latexes. Benzene is also used in the manufacture of cumene (isopropyl benzene), from which comes 96% of domestic phenol production, and cyclohexane, important in the manufacture of nylon. Small amounts find uses

in the manufacture of detergents, insecticides, antioxidants, adhesives, and pharmaceuticals. Benzene is extracted from the BTX fraction obtained from catalytic reforming of naphtha.

Toluene

More than 90% of toluene (methylbenzene) is directed to the production of gasoline. Of the remaining amount, over half goes to the production of benzene, while smaller amounts are used as solvent in the production of paints and coatings and other miscellaneous products. Toluene is extracted from the BTX fraction obtained from catalytic reforming of naphtha.

Xylenes

Mixed xylenes (dimethylbenzene) consist of ortho-, meta-, and para-isomers. Separation of these isomers provides starting material for phthalic anhydride, used in plasticizers, isophthalic acid, a component of polyester resins, and dimethyl terephthalate and terephthalic acid, intermediates in the production of polyterephthalates. Mixed xylenes are also employed as solvents and in the formulation of adhesives and rubber. Xylenes are extracted from the BTX fraction obtained from catalytic reforming of naphtha.

Acetic Acid

Over 60% of acetic acid (ethanoic acid) production is used in the manufacture of vinyl acetate, the basis of white glue, laminating wallboard, and latex paint. Polymers derived from vinyl acetate find applications in the manufacture of safety glass, film products, and hot melt adhesives. About 15% is consumed in the production of acetic anhydride, most of which is converted to cellulose acetate, which is used to manufacture textile fibers, plastics, and films. About 10% of acetic acid demand supports the production of ester solvents used in the manufacture of inks, paints, and coatings. Another 10% is used to produce terephthalic acid (1,4-benzene dicarboxylic acid) and dimethyl terephthalate (dimethyl 1,4-benzene dicarboxylate) for the manufacture of fibers, resins, paints, coatings, and plastics. The production of acetic acid from fossil fuels begins with reforming of natural gas or gasification of coal to syngas. As described in Chapter 8, syngas is catalytically converted to methanol followed by catalytic carbonylation (i.e., synthesis of a carbonyl compound by the addition of carbon monoxide) to acetic acid.

Acetic acid is a metabolite from the fermentation of a variety of sugars by several organisms, including *Acetobacter aceti*, *Clostridium thermoaceticum*, and *Pachysolen tannophilus*. Acetic acid is also a major project from pyrolysis of lignocellulosic biomass. However, acetic acid from biorenewable resources is not presently cost-effective compared to production from fossil fuels.

Formic Acid

Demand for formic acid (methanoic acid) is evenly distributed in the manufacture of rubber chemicals, aluminum and nickel catalysts, leather and tanning, textiles, and other miscellaneous industries. Partial oxidation of butane, obtained from natural gas liquids, yields a mixture of carboxylic acids from which formic acid is separated.

Formic acid and three other carboxylic acids (acetic, glyceric, and lactic) can be produced by mild alkaline oxidation of dilute aqueous solutions of xylose, representing a possible path for production of biobased products. Carboxylic acids are highly water soluble, which impedes the recovery and commercial exploitation of this process.

Propionic Acid

Up to 30% of propionic acid (propanoic acid) is used to preserve grain. Another 25% is converted to sodium and calcium salts of the acid, which are used as food and feed preservatives. Production of carboxylic acid herbicides consumes another 15% with the balance used for cellulose plastics, pharmaceuticals, and solvents. Propionic acid is obtained by carbonylation of ethylene, which is derived from the pyrolysis of ethane, a constituent of natural gas.

Propionic acid is a metabolite from the fermentation of various sugars by various microorganisms including *Clostridium* species and *Propionibacterium shermanii*. The commercial production of propionic acid by fermentation is not economically viable at present.

Acrylic Acid

Acrylic acid (2-propenoic acid) is an unsaturated liquid acid that is widely used to produce acrylic esters, which are useful in the production of latexes, textiles, adhesives, sealants, and inks. Acrylic esters, which command 72% of production in acrylic acid, have increasing application as cross-linking agents for producing hard, cured surfaces. Non-ester polymers of acrylic acid have applications as flocculants, dispersants, and thickeners. New types of polyacrylic acids have recently been developed as superabsorbents such as are used in disposable diapers. A two-stage oxidation process is used to produce acrylic acid from propylene.

Succinic Acid

Succinic acid (butanedioic acid) is a crystalline dicarboxylic acid found as a common metabolite in many plants, animals, and microorganism. It is a specialty chemical with applications in food and pharmaceutical products, surfactants and detergents, biodegradable solvents and plastics, and ingredients to stimulate animal and plant growth. Its production from fossil resources begins by oxidizing butane to maleic anhydride (2,5-furandione), which is followed by reduction to succinic

anhydride (dihydro-2,5-furandione) and ring opening hydrolysis to give succinic acid.

Although a biodegradable product, for it to qualify as a biobased product, it must be produced from biorenewable resources. Efforts are under way to develop a commercial process for fermenting it from cornstarch.

Butanol

Butanol is a four-carbon alcohol (C_4H_9OH) of either of two isomeric forms (1-butanol or 2-butanol) derived from normal butane. Butanol has been suggested as an oxygenated fuel for blending with gasoline, with distinct advantages over methanol and ethanol. The energy content of butanol is closer to that of gasoline and it has no compatibility or miscibility problems with gasoline. Butanol is water tolerant; thus, it can be transported in gasoline blends by pipeline without danger of phase separation due to moisture absorption. Butanol is also a feedstock for production of butyl butyrate, often touted as a green solvent. Butanol is obtained from butane, which is extracted from natural gas liquids. Various species of *Clostridium* can ferment butanol from sugars. Like many other fermentation processes, recovery of the metabolite is a key challenge to the economics of biobased butanol.

Phenol

About 35% of phenol production goes into phenolic resins, which are primarily employed as adhesives for plywood, laminates, and insulation. About 10% of these resins are used in molding compounds for heat-resistant materials. Another 35% of phenol production supports the manufacture of polycarbonate resins, a common material in the construction of automobiles, appliances, and milk bottles, and epoxy resins, a surface coating for electronic circuit boards and a component of advanced composites. Smaller amounts of phenol are employed to manufacture nylon carpet and aniline, a useful chemical in the manufacture of inks, dyes, herbicides, and other products. Phenol is used in the production of salicylic acid, the active component of aspirin and flavorings. Phenol from petrochemicals is derived by oxidizing cumene (isopropyl benzene), which is synthesized from benzene and propylene.

6.5.2 Chemicals Produced from Biorenewable Resources

Several oxygenated organic compounds are commercially produced from biorenewable resources. In large part, these biobased products can compete in the market because synthesis routes from fossil resources to yield a comparable product have not emerged. These exceptions include lactic acid and furfural. Also commercially competitive are some cellulose derivatives, for which consumers value the intrinsic properties of the resulting biobased synthetic fibers.

Furfural and Other Furans

Furfural (2-furaldehyde) is a commercially important solvent used in the manufacture of pesticides, synthetic resins, and nylon. It is also used to produce furfuryl alcohol, which in turn is used to produce "furan resins," important in the metal casting industry to form cores and molds. Smaller quantities of these resins are used to produce corrosion resistant grouts, mortars, joints, and valves. Some furfural is converted to tetrahydrofuran, a solvent in the resins and plastics industry.

Furfural is produced by a series of acidic dehydrations of pentoses obtained from hemicellulose-rich agricultural materials such as corncobs, oat hulls, and peanut shells. Although classified as secondary processing of biorenewable resources, in practice the dehydration of pentose occurs simultaneously with the hydrolysis of hemicellulose in a single reactor known as a digester. Sulfuric acid and biomass are blended and reacted with steam in the digester. Furfural, which boils at 160°C, appears as vapor, which exits with steam leaving the reactor. Distillation yields furfural and a wastewater stream containing about 1% acetic acid.

Furfural, illustrated in Figure 6.8a, is a member of the furan compounds, the heterocyclic aromatic series characterized by a ring structure composed of one oxygen atom and four carbon atoms. The reactivity of the furan ring allows a wide range of synthesis options. Furfural is converted to furan (Figure 6.8b), the simplest member of this series, by catalytic decarbonylation, or to furfuryl alcohol (Figure 6.8c) by hydrogenation of the aldehyde group. Furan can be converted to tetrahydrofuran (Figure 6.8d) by catalytic hydrogenation. Furfuryl alcohol can be hydrogenated to tetrahydrofurfuryl alcohol (Figure 6.8e). From tetrahydrofuran and tetrahydrofurfuryl alcohol, a wide variety of derivatives can be obtained. The ring cleavage chemistry of furan suggests the basis for synthesis of a variety of other chemicals, as well, including *n*-butanol, 1,3-butadiene, styrene, adipic acid, maleic anhydride, 1,4-butanediol, and *y*-butyrolactone. Both furan and furfural have been converted to maleic anhydride.

Lactic Acid

Lactic acid (2-hydroxypropanoic acid) is a common metabolite in animals, plants, and bacteria. It is widely used in the food industry as a preservative and flavoring. Esterification with ethanol produces ethyl lactate, a solvent that also serves as a chemical intermediate. Lactate can be converted to polylactic acid (PLA) resin used

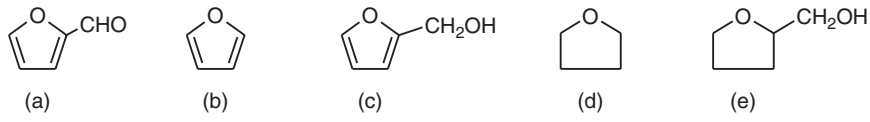


FIG. 6.8 Furan compounds synthesized from pentose: (a) furfural; (b) furan; (c) furfuryl alcohol; (d) tetrahydrofuran; (e) tetrahydrofurfuryl alcohol.

in the production of biodegradable plastic that has properties that are competitive with plastics made from polyethylene and polystyrene. Although manufacturing processes have been developed for producing lactic acid from either fossil resources or biorenewable resources, economics are increasingly favoring the use of biorenewable resources. In this case, lactic acid is produced by fermentation of glucose.

Gluconic Acid

Gluconic acid (2,3,4,5,6-pentahydroxyhexanoic acid) is converted to the chelating agent sodium gluconate, useful in removing metal ions, especially calcium, magnesium, iron, and aluminum. As such, it finds application in metal cleaning as well as equipment cleaning in the dairy and food service industries. It also has miscellaneous applications in textile, pharmaceutical, and health food industries. Gluconic acid is produced in almost quantitative yields by the oxidation of glucose in air or oxygen.

Xylitol

The pentahydric alcohol known as xylitol ($C_5H_{12}O_5$), like sorbitol and mannitol, is used as a sweetener and humidity control agent, although it has a relatively small market. It is produced from the hemicellulose fraction of birch wood. Acid hydrolysis of the finely milled wood yields the five-carbon sugar xylose and oligomers, which is removed by a hot water wash. Hydrolysis of this stream yields additional xylose, which is separated from other pentoses. Combination of xylose with hydrogen in the presence of a nickel catalyst hydrogenates the aldehyde group of xylose to yield xylitol at very high yields. Processes have also been patented for extracting the necessary xylose from corncobs and bagasse. Fermentative routes to xylitol production have also been developed. One strain of yeast, *Aureobasidium*, hydrolyzes corn fiber to xylose, while another strain, *Pichia guilliermondii*, ferments the xylose into xylitol.

Sorbitol

Sorbitol is a faintly sweet alcohol ($C_6H_{14}O_6$) derived from the catalytic hydrogenation of sucrose. Its use in toothpaste, cosmetics, and toiletries represents 32% of total domestic consumption of sorbitol. Its hygroscopic properties are employed as emollient in creams and lotions, while its cooling, sweet taste makes it suitable for mouthwashes. Sorbitol is classified as a semi-natural, nutritive sweetener with 60% of the sweetness of sucrose; thus, it is used as a confection in foods and snacks, especially mints and gums. It has applications as a bulking agent, peeling aid, and flavoring agent in the food industry. About 17% of sorbitol production is employed in the manufacture of vitamin C. Esterification of sorbitol results in a surfactant useful as a lubricant, softener, plasticizer, and anti-static agent. Sorbitol is made in very high yield by catalytic hydrogenation of isoglucose, which is produced by molybdate-catalyzed isomerization of starch-derived glucose.

Mannitol

Mannitol ($C_6H_{14}O_6$), an isomer of sorbitol, is also a slightly sweet alcohol. It finds similar applications as sorbitol, although it has a smaller market. Mannitol is a coproduct of the production of sorbitol, representing about 30% of the yield from isoglucose.

Cellulose Derivatives

Cellulose can be manipulated to produce a variety of products. Most prominent is synthetic fibers of rayon, derived from regenerated cellulose. Rayon has found application in top-weight apparel, home furnishings, and non-woven materials. Cellulose acetate fibers, another product derived from cellulose, has wide application in the textile market for soft, dyeable apparel. Cellulose ester was the first thermoplastic, widely used to manufacture tools, toys, and automobile parts; however, this market has declined in the face of competition from petroleum-derived plastics. Similarly, the cellulose ether known familiarly as cellophane was widely used by the packing industry until less costly petroleum-based products were developed. Because cellophane is biodegradable, its prospects might improve in the future. Most of these cellulose derivatives come from wood pulp.

6.5.3 Chemicals with Potential for Production from Biorenewable Resources

Levulinic Acid

Levulinic acid (4-oxopentanoic acid) has not been commercially exploited, but it may prove useful in the production of antifreeze, fuel additives, plasticizers, synthetic resins, and hydraulic brake fluids. Hydrogenation of levulinic acid yields valeric g-lactone, an excellent solvent. Levulinic acid is produced by high-temperature acid hydrolysis of hexoses (with the coproduction of formic acid) or acid treatment of tetrahydrofurfuryl alcohol.

Levoglucosan

Levoglucosan is an anhydrosugar derived from cellulose or starch. It is a chiral compound with potential as a building block for the production of pharmaceuticals, insecticides, new polymers, and sugar alcohols. It is currently an expensive specialty chemical, but process improvements under development could drastically reduce its cost and open the way for commercial applications. Levoglucosan is produced by the fast pyrolysis of acid-treated lignocellulose with yields in the range of 20–30%. Separation techniques to yield a high purity product still need to be developed.

Hydroxyacetaldehyde

Hydroxyacetaldehyde is a carbonyl compound not currently produced commercially. However, it is a potential replacement to another carbonyl compound,

glyoxal (1,2-ethanedione), which is an important cross-linking agent in the manufacture of resins, currently produced from fossil resources. Hydroxyacetaldehyde is a coproduct in the pyrolysis of lignocellulose, with yields of about 10%.

Starch Plastics

The earliest commercial "starch plastics" were starch-filled polyethylene, a composite derived from both fossil and biorenewable resources. Although they were "biodisintegratable," with the starch breaking down to leave a recalcitrant polyethylene residue, they were not biodegradable in the sense of completely breaking down in relatively short time frames of a few weeks or months.

More advanced starch plastics chemically modify starch to produce polymeric material that completely degrades. For example, modification of hydroxyl groups during starch esterification yields starch esters that are thermoplastic and water resistance. Starch ester resin reinforced with natural fibers has properties comparable to general-purpose polystyrene. Formulated with plasticizers and other additives, starch ester yields resins suitable for injection-molded products.

Acetylated Wood

Acetylated wood undergoes a chemical treatment that improves dimensional stability (i.e., reduced swelling and shrinkage with moisture content) and resistance to biological degradation. The chemical treatment is a process of esterification, which can be accomplished in several different ways. Most commonly, acetic anhydride (ethanoic anhydride) is used to prepare acetylated wood, which produces acetic acid as a byproduct and unreacted acetic anhydride, which can be recycled to the acetylation reactor.

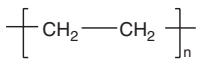
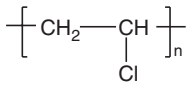
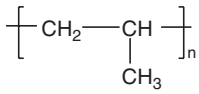
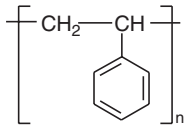
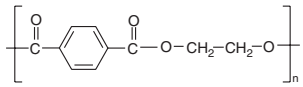
Polyhydroxybutyrate/Polyhydroxyvalerate

Polyhydroxybutyrate (PHB) and its copolymers with polyhydroxyvalerate (PHV) are melt-processable, semi-crystalline thermoplastics polyesters that are stable under everyday conditions but degrade slowly in the body and when composted or landfilled. The PHB homopolymer is stiff and rather brittle with mechanical properties resembling those of polystyrene, although it is less brittle and more temperature resistant. Copolymers are preferred for general purposes, while the homopolymer is expected to have applications in the medical and biological fields. These polymers can be prepared microbiologically from glucose or syngas. Their production in transgenic plants has also been demonstrated.

6.5.4 Synthetic Biopolymers

Polymers are used in the manufacture of a wide variety of products. Most are derived from petroleum rather than biorenewable resources. This is not because polymers are rare in nature. In fact, biologically derived polymers (biopolymers) are

Table 6.4 Common petroleum-derived polymers

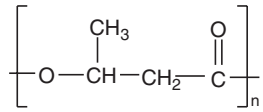
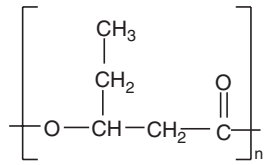
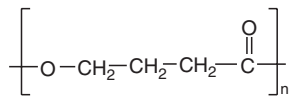
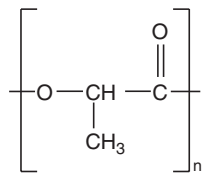
Name	Formula	Applications	Market Share[a]
Polyethylene		LDPE—food packing, grocery bags, trash bags, squeeze bottles, industrial sheeting HDPE—milk judges, laundry detergent bottles, containers, sporting goods, pipes, insulation, toys	36%
Poly(vinyl chloride)		Flexible PVC—clear film and foam for packaging, floor and wall coverings, garden hose, electrical insulations, "vinyl" Rigid PVC—credit cards, pipes, building materials and components	20%
Polypropylene		Packaging film, food containers, bindings, bottles, beverage crates; coatings, luggage, laboratory ware, molded automobile parts, appliances	19%
Polystyrene		Packaging for meat, pastry, candy; expanded polystyrene (Styrofoam) used for food containers; furniture, toys, disposable dishes and utensils	9%
Poly(ethylene terephthalate)		Beverage bottles, audio and video tape	6%

Source: Stevens, E.S. (2002) *Green Plastics: An Introduction to the New Science of Biodegradable Plastics*. Princeton, NJ: Princeton University Press.[a]Includes both thermoplastics and thermosets.

ubiquitous in nature and include polysaccharides, lignin, proteins, and polyesters. These were widely exploited in the production of manufactured product until the rise of petrochemistry, which provided inexpensive chemical building blocks from petroleum for the synthesis of versatile synthetic polymers, including polyethylene, polyvinyl chloride, polypropylene, and polystyrene (see Table 6.4). Biopolymers in the form of natural fibers continue to have many important commercial products including paper, textiles, and construction materials, as described in the next section, but they do not have the versatility of application of many synthetic polymers.

It is possible to make synthetic polymers from biorenewable resources. These synthetic biopolymers fall into two categories. The first are chemically and functionally indistinguishable from the petroleum-derived polymers listed in Table 6.4. They are produced by first converting the biorenewable resources into the same building blocks used for constructing the petroleum-derived polymers: ethylene, vinyl, propylene, and styrene, for example. From there, the synthesis route is

Table 6.5 Synthetic biopolymers

Name	Formula	Applications
Poly-3-hydroxybutyrate		Biocompatible and biodegradable polyester (PHB): copolymer with PHV can yield properties resembling polyethylene or polypropylene. Products include bottles, disposable razors, eating utensils, credit cards, controlled drug release, surgical sutures
Poly-3-hydroxyvalerate		Biocompatible and biodegradable polyester (PHV): copolymer with PHB can yield properties resembling polyethylene or polypropylene. Products include bottles, disposable razors, eating utensils, credit cards, controlled drug release, surgical sutures
Poly-4-hydroxybutyrate		Biocompatible and biodegradable polyester: copolymer with PHV can yield properties resembling polyethylene or polypropylene. Products include bottles, disposable razors, eating utensils, credit cards, controlled drug release, surgical sutures
Poly(lactic acid)		Water insoluble polyester: flocculating agent; synthetic fibers for textiles, compost bags, disposable eating utensils, sport equipment, paper coatings, film wrap, drug delivery systems, orthopedic materials

Source: Stevens, E.S. (2002) *Green Plastics: An Introduction to the New Science of Biodegradable Plastics*. Princeton, NJ: Princeton University Press.

identical to that of the petroleum-derived polymers. The second category consists of synthetic polymers produced from biorenewable resources that are chemically distinct from petroleum-derived polymers but share similar functionality in applications. As shown in Table 6.5, these include poly-3-hydroxybutyrate, poly-3-hydroxyvalerate, poly-4-hydroxybutyrate, and polylactic acid.

6.6 Natural Fibers

Plant fibers can be used in the manufacture of textiles, paper products, and composite materials. Cotton fibers are widely employed in the manufacture of textiles, while hardwood fibers dominate the markets for paper products and composite

Table 6.6 Comparison of properties of plant fibers to synthetic fibers

	Specific Gravity	Specific Tensile Strength (GPa)	Cost ($/ton)
Plant fibers	0.6–1.2	1.60–2.95	200–1000
Glass	2.6	1.35	1500–2000
Kevlar	1.4	2.71	4000–6000
Carbon	1.8	1.71	8000

Source: Bolton, A.J. (1994) Natural fibres for plastic reinforcement. *Materials Technology*, 9, 12–20.

materials. Historically, herbaceous plants such as bamboo, hemp, jute, kenaf, and sisal, and crop residues, such as wheat straw and cornstover, have been sources of non-woody fiber for the production of paper and composite materials, especially during times of wood scarcity. However, the relatively higher cost of collecting and storing non-woody plant fibers and their slightly inferior properties have favored the use of wood fibers.

Non-woody plant fiber accounts for a small fraction of worldwide pulping capacity, with wheat straw accounting for more than 40% of this capacity. Much of this capacity exists in emerging markets: China, India, Pakistan, and Mexico, among others. The combination of increasing standard of living and growing shortage of wood in these countries is expected to further boost the prospects of non-woody fiber in the pulp and paper industry.

A composite is a material consisting of fibers reinforced by an adhesive matrix. In general, composites contain a large volume fraction of adhesive to avoid the occurrence of voids, which markedly degrades the strength of composite materials. Because plant fiber composites have been targeted at large volume markets, they rarely contain more than 3–12% adhesive to reduce the cost of the final product. This can be done because the polysaccharide and phenolic polymers from which plant fibers are constructed are very reactive, which makes them readily bond to adhesives compared to synthetic fibers. The inevitable presence of voids means that these products will be relegated to relatively low value applications unless developers are able to capitalize on unique properties imparted by the use of plant fibers in the composites.

As shown in Table 6.6, plant fibers can be competitive in terms of weight, specific tensile strength, and cost. Plant fibers also provide environmental advantages: less energy is consumed in producing these fibers and the resulting composites can be burned for energy at the end of the life of the product.

One of the most important features of fibers is their aspect ratio, that is, the ratio of fiber length to diameter. Plant fibers have two distinct aspect ratios: one for individual fibers and another for fiber bundles that occur naturally in plant materials, which can be extracted intact from certain non-wood plants, such as sisal, hemp, and flax. Most individual fibers have aspect ratios in the range of 100–200 with a few notable exceptions: hemp at 550, flax at 1500, cotton at 2000,

and ramie at 4000. The aspect ratio of fiber bundles varies from about 100 to over 4000, depending on the success of extracting the bundles from plant tissue. Short plant fibers are attractive as reinforcement in molding compounds and injection moldings, while longer fibers find application where anisotropy is an important property of the composites.

Two other properties of fibers will be mentioned that favor plant fibers in certain applications. Long fibers or fiber bundles can be aligned in a process known as carding in the textile industry. This ability to control fiber orientation allows anisotropic properties of strength and stiffness to be exploited. The other property, characteristic of long plant fibers, is known as drape: the ability of fabrics to flow over and follow complex shapes. This property is important in the molding of composites into complex shapes.

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CHAPTER

7

Biochemical Processing of Carbohydrate-Rich Biomass

7.1 Introduction

A variety of processes have been developed for converting biomass into chemicals and fuels. These can be generally classified as biochemical or thermochemical processing of biomass. Biochemical processing utilizes enzymes and microorganisms to convert carbohydrate-rich biomass into desired products, while thermochemical processing uses heat and catalysts to convert lignocellulosic biomass into products. Sometimes biochemical and thermochemical processes are combined into a hybrid processing scheme. This chapter covers biochemical processing of carbohydrate-rich biomass, while Chapter 8 considers thermochemical processing and hybrid processing of lignocellulosic biomass. Lipid-rich feedstocks, which are processed in ways quite distinct from carbohydrate-rich and lignocellulosic biomass, are covered in Chapter 9.

Biochemical processes considered for the conversion of carbohydrate-rich biomass into fuels and chemicals include fermentation of sugars and starches; acid and enzymatic hydrolysis of lignocellulose to simple sugars followed by subsequent fermentation; and consolidated bioprocessing (CBP) of lignocellulose.

7.2 Fermentation of Sugars and Starches

Fermentation is a biological process in which enzymes produced by microorganisms catalyze energy-releasing reactions that break down complex organic substrates. Anaerobic conditions, characterized by the exclusion of oxygen, are most common, but aerobic processes, in which oxygen is present, are also possible. The French chemist Louis Pasteur established the field of microbiology during his efforts to help the brewery industry improve its product. He introduced the word

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fermentation from the Latin *fermentare* (to boil) to describe microbial activity that releases gas as foam.

Fermentation can produce a wide variety of chemicals although most of them are organic acids and alcohols. Most microorganisms used in commercial fermentations require six-carbon sugars (hexoses) or disaccharides as substrates although the microbial world contains organisms that can breakdown virtually any organic compound. Recent technological advances have made possible the fermentation of five-carbon sugars (pentoses).

Several factors limit the use of fermentation technology in the production of chemicals. Production rates by microorganisms in aqueous media of low solids volume are inherently low. The microorganisms are both sensitive to inhibitors and operating conditions, especially temperature and pH. Most fermentations require aseptic conditions, which can be difficult to achieve in large-scale operations. Recovery of water-soluble products from dilute solutions can be expensive. Effluent usually contains high biochemical oxygen demand (BOD), which requires wastewater treatment before discharge.

A major emphasis in the fermentation industry is the production of ethanol, which is marketed to both fuel and beverage industries. Table 7.1 lists ethanol fermentation yields for a variety of carbohydrate feedstocks. The maximum theoretical yield of ethanol is 0.51 (mass ethanol/mass carbohydrate, corresponding to 51% of the carbohydrate converted to ethanol on a mass basis), the balance being carbon dioxide. Typically, about 5–12 wt% of the carbohydrate is converted to cells; thus, not more than 47 wt% of the fermented carbohydrate is converted to

Table 7.1 Ethanol yields from various biorenewable resources

Feedstock	Yield (L/ton)
Apples	64
Barley	330
Cellulose	259
Corn	355–370
Grapes	63
Jerusalem artichoke	83
Molasses	280–288
Oats	265
Potatoes	96
Rice (rough)	332
Rye	329
Sorghum (sweet)	44–86
Sugar beets	88
Sugarcane	160–187
Sweet potatoes	125–143
Wheat	355

Source: Klass, D.L. (1998) *Biomass for Renewable Energy, Fuels, and Chemicals*. Academic Press.

ethanol. Of course, other products can also be produced by fermentation, which are described later in this chapter.

The following sections explore the technologies by which carbohydrates, including sugar, starch, and lignocellulose, are converted to coproducts. Regardless of the carbohydrate, the following processes are involved: release of simple sugars from the carbohydrate, fermentation to organic acids or alcohols, distillation of the fermentation broth to recover the fermentation products, and utilization of coproducts. Differences among the carbohydrates are how simple sugars are released and how coproducts are utilized.

7.2.1 Sugar Crops

Traditional sugar crops used for fermentation include apples, grapes, other fruits, sugarcane, sugar beets, and sweet sorghum. Molasses, which is the residual syrup remaining from crystallization of sugar from sugarcane and sugar beets, is also a common feedstock. Even pulp and paper mill sludges contain as much as 40–50 wt% glucose. These sugars can be directly fermented by the yeast *Saccharomyces cerevisiae*, which contains enzymes that hydrolyze disaccharides to simple sugars and catalyze the fermentation of four hexoses: glucose, mannose, fructose, and galactose.

The most important sugar crop for production of biofuels is sugarcane. Traditionally, the leaves and tops of the sugarcane plant are burned or left in the field, while the stalk is transported to a sugar mill. As shown in Figure 7.1, the conversion of sugarcane into ethanol consists of four major processes: milling the cane, filtration/evaporation of the syrup, fermentation of the sugar, and distillation of the ethanol. Milling is designed to separate sugar, making up 20–30 wt% of the cane, from the fibrous part of the plant. The cane is chopped and shredded with revolving blades, and washed with hot water to produce a sugar-rich juice and a fibrous residue, known as bagasse. Bagasse can be used as boiler fuel, containing one-third of the total energy found in sugarcane, and is used by Brazilian ethanol plants as their primary source of electricity as well as heat for evaporation and distillation processes in the plant. After the bagasse has been separated, the juice is filtered multiple times, pasteurized, and evaporated until a mixture of crystalline sugar and molasses remains. The sugar content of the juice is adjusted to less than 22 wt% of sugar to avoid inhibition of yeast activity. Nutrients such as ammonium sulfate are added as needed to make up deficiencies in the original feedstock. The broth is allowed to ferment for up to 12 hours, producing a liquid similar to wine with an alcohol content of up to 10%. Finally, this liquid is distilled to produce 100% ethanol.

The cost of building a modern sugarcane ethanol plant capable of producing 50 million gallons per year was $150 million in 2008 with half of the processed sugarcane being used to produce crystalline sugar and the other half to produce

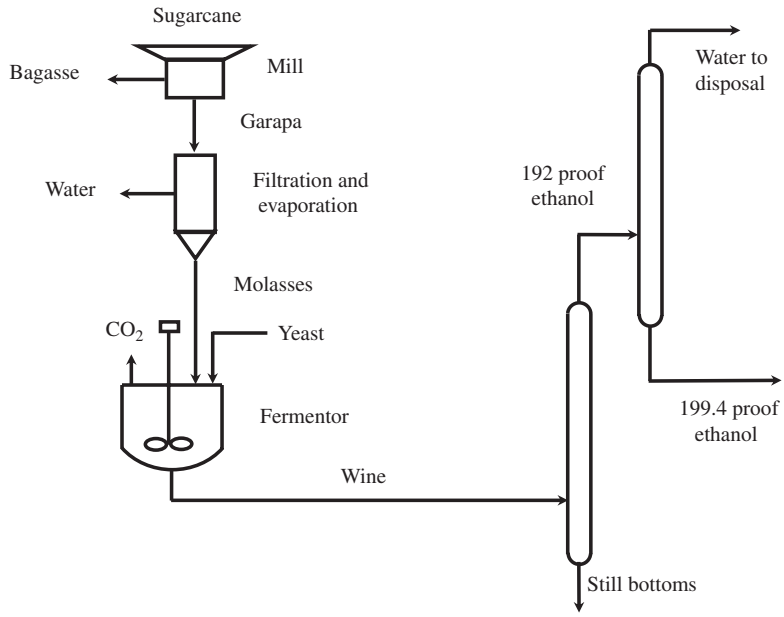

FIG. 7.1 Sugarcane processing to sugar and ethanol.

ethanol. These plants produce roughly 20 gallons of ethanol per ton of sugarcane processed. The cost of production largely depends on the price of sugarcane, which averaged $10.40 per ton in 2005, or $0.54/gallon. After including other expenses like invest and transportation costs, the ultimate cost of production varies from $0.63 to $0.76 per gallon of ethanol, which is 20–80% less expensive than grain ethanol. Because a gallon of ethanol contains only 67% of the energy that a gallon of gasoline contains, this cost is more accurately portrayed as $0.95–$1.13 per gallon of gasoline equivalent, making it competitive with gasoline at $40–$50 per barrel prices.

The ability to use bagasse, the plant fibers that remain after syrup has been pressed from sugarcane, as boiler fuel makes ethanol from sugarcane relatively fossil-fuel efficient. Whereas the net energy balance—the ratio of the energy in a unit of ethanol divided by the fossil fuel energy required to produce it—for corn-based ethanol is 1.3, the balance for sugarcane-based ethanol ranges between 8.2 and 10, due in large part to the energy self-sufficiency of many Brazilian ethanol plants. This use of bagasse also contributes to roughly a 90% decrease in greenhouse gas emissions resulting from using ethanol instead of gasoline.

Brazil has built a transportation sector that relies heavily upon ethanol fermented from sugar crops. However, in the United States, sugar subsidies make it too expensive for production of ethanol.

7.2.2 Starch and Inulin Crops

Starch is a polymer that accumulates as granules in many kinds of plant cells where they serve as a storage carbohydrate. Mechanical grinding readily liberates starch granules. The hydrogen bonds between the basic units of maltose in this polymer are easily penetrated by water, making depolymerization and solubilization relatively easy.

Hydrolysis, the process by which water splits a larger reactant molecule into two smaller product molecules, is readily accomplished for starch. Acid-catalyzed hydrolysis in "starch cookers" at temperatures of 150–200°C proceeds to completion in seconds to minutes. In recent years, enzymatic hydrolysis has supplanted acid hydrolysis due to higher selectivity.

Starch is a glucose polymer with two main components: amylose, a linear polymer of glucose with α-1,4 linkages, and amylopectin, a branched chain including α-1,6 linkages at the branch points. Thus, enzymatic saccharification of starch requires two enzymes. The enzyme amylase hydrolyzes starch to maltose in a process known as liquefaction. The enzyme maltase hydrolyzes maltose into glucose in a process known as saccharification. The consumption of either acid or enzymes for starch hydrolysis is less than 1:100 by weight, making the cost of hydrolysis only a small part of the cost of starch fermentation.

Inulin, like starch, is a storage carbohydrate, but its basic unit is fructose rather than glucose. It is commonly found in tuber crops such as dahlias and Jerusalem artichokes. It is also easily depolymerized and solubilized by both acid- and enzyme-catalyzed hydrolysis. Although potentially an important fermentation feedstock, reversion of fructose to undesired oligofructosans and the lack of widespread cultivation of inulin crops have limited their use.

Cereal grains, such as corn, wheat, and barley, are the most widely used sources of starch for fermentation. The cell walls of grains must be disrupted to expose starch polymers before they can be hydrolyzed to fermentable sugars (i.e., monosaccharides and disaccharides). Grain starch consists of 10–20 wt% amylose and 80–90 wt% amylopectin, both of which yield glucose or maltose on hydrolysis. Although the amylose is water soluble, the amylopectin is insoluble, requiring a "cooking" operation to solubilize it prior to hydrolysis.

Cereal grains also contain other components, such as protein, oil, and fiber, which may be of sufficient value to recover along with the starch. For example, gluten, a mixture of plant proteins occurring in cereal grains, chiefly wheat and corn, is of value as an adhesive and animal feed. If these components are to be separately recovered, extensive pretreatment, known as wet milling, is required before the starch is hydrolyzed and fermented. Under some circumstances, separation of plant components is not economically justified; simpler dry milling is employed to release starch polymers and the whole grain is fermented. Of the 50.5 GL (13.3 billion gal) of fuel ethanol annually produced from corn starch in the United

States, more than 80% comes from dry milling plants, while the remaining 20% is the result of wet milling.

The pretreatments of dry milling and wet milling are distinct in their operations, as detailed in the following paragraphs. The subsequent processes of hydrolysis, fermentation, and distillation, however, are very similar for the two kinds of corn milling plants. Either relatively pure starch from wet milling or a starch-rich "mash" from dry milling is treated with the enzyme amylase and heated to around 93°C to partially hydrolyze the starch in a process called liquefaction to form a mixture of oligosaccharides and polysaccharides known as dextrin. The mash of dextrin is cooled to between 60°C and 70°C, the pH adjusted to 3–5, and the enzyme glucoamylase is added for the final step of hydrolysis, known as saccharification, which yields glucose.

The capital investment for dry milling is less than that for a comparably sized wet milling plant. However, the higher value of its by-products, greater product flexibility, and simpler ethanol production can make a wet milling plant a more profitable investment.

7.2.3 Dry Milling of Corn

Dry milling is essentially a simple grinding procedure. When employed in the food industry, a series of grinding and screening steps are employed. First, the corn is cleaned and then conditioned for 24 hours to increase moisture content to 15–20 wt%. The kernels then pass through roller mills or crushers to separate the kernel into germ, endosperm, and fibrous hull by gravity. The germ contains 18–25 wt% oil, which can be recovered by solvent extraction. The starchy particles of the endosperm can be further ground and sieved to three products distinguished by their particle size: flour, cornmeal, and grits. About 75 wt% of the kernel becomes flour, cornmeal, or grits, 5 wt% is recovered as oil, and 11 wt% is used as fibrous feed. The starchy components can be used in food products or saccharified for fermentation.

For production of fuel ethanol by dry milling, illustrated in Figure 7.2, separation into various products is not necessary. Kernels are ground in a roller mill to grain meal consistency to expose the starch. The meal is slurried with water to form a mash, which is fermented to ethanol. The fibrous residue remaining upon completion of fermentation is recovered from the base of the beer stripping column, mixed with yeast and other unfermented residues, and dried to a coproduct known as distillers' dried grains and solubles (DDGS). This coproduct, containing about 25 wt% protein and residual oil, is a valuable feed for cattle. Profitability of a corn-to-ethanol plant is strongly tied to the successful marketing of DDGS.

A typical dry milling plant will produce about 10.6 L (2.8 gal) of ethanol per bushel of corn processed. Yields of coproducts per bushel of corn are about 7.1 kg (15.7 lb) of DDGS and 7.5 kg (16.5 lb) of carbon dioxide evolved from

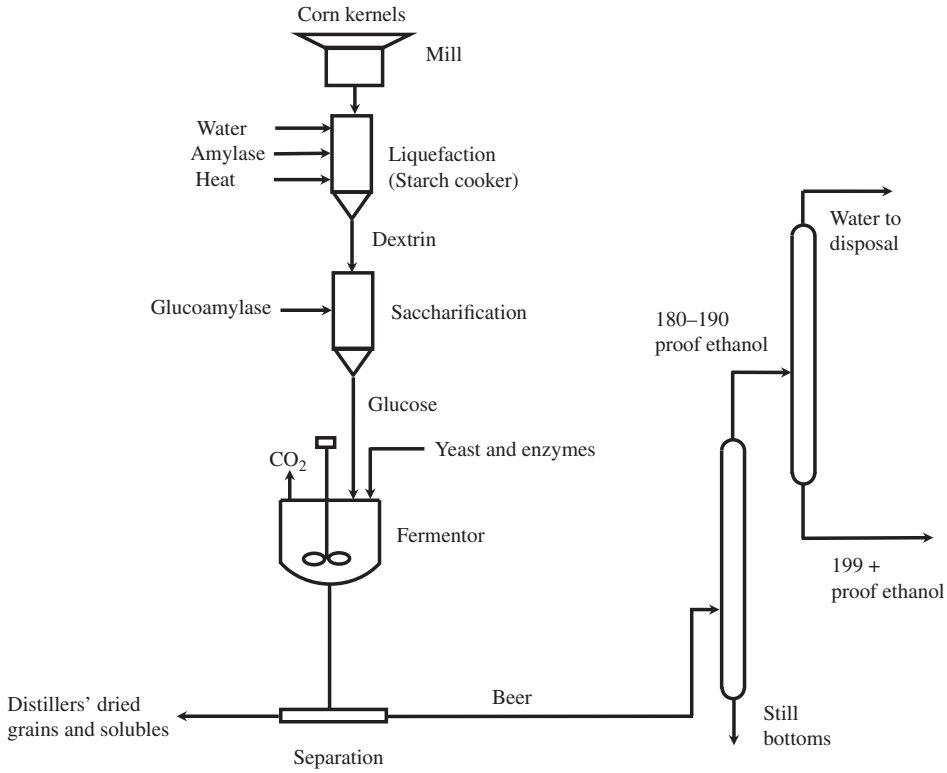

FIG. 7.2 Dry milling of corn.

fermentation, the latter of which can be sold to the carbonated beverage industry. As a rule of thumb, the three products are produced in approximately equal weight per bushel, with each accounting for approximately one-third of the initial weight of the corn.

7.2.4 Wet Milling of Corn

Wet milling has the advantage that it separates plant components into carbohydrate (starch), lipids (corn oil), a protein-rich material (gluten), and fiber (hulls). This gives a company access to higher value markets as well as provides flexibility in the use of starch as a food product or in the production of fuel ethanol.

The wet milling process is illustrated in Figure 7.3. The corn is cleaned and then conveyed into steep tanks where it is soaked in a dilute solution of sulfur dioxide for 24–36 hours, which swells and softens the corn kernels. Some of the protein and other compounds are dissolved in the resulting corn steep liquor, which represents an inexpensive source of nitrogen and vitamins.

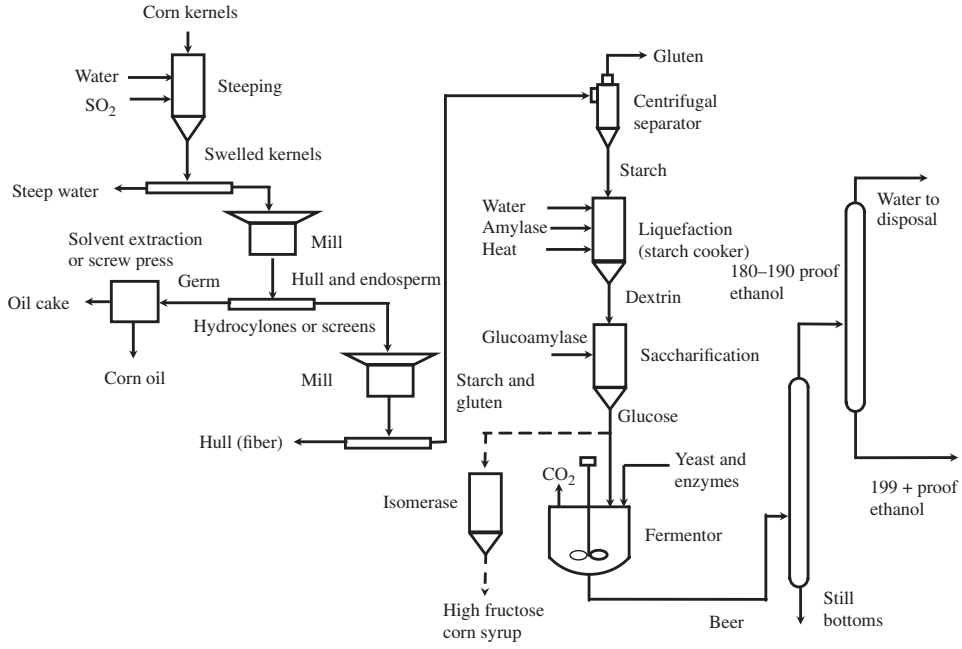

FIG. 7.3 Wet milling of corn.

After separating the corn from the steep liquor, the wet kernels are coarsely ground to release the hull and germ from the endosperm. Hydrocyclones or screens separate the germ from the rest of the components. After drying, oil is extracted from the germ by either solvents or a screw press, leaving a residual oil cake. The hull and endosperm pass through rotating disc mills that grind the endosperm into fine fractions of starch and gluten, while the hull yields coarser fiber particles, which can be screened out from the finer fractions. Centrifugal separators separate the lighter gluten from the starch.

The starch can be used directly as a food product or for industrial manufacturing processes, especially papermaking. The starch can also be converted to monosaccharides for the production of food or fuel, depending on relative market demand. Saccharification by amylase enzymes yields corn syrup, a glucose solution that can be directly fermented to fuel ethanol. Alternatively, treated with isomerase enzymes, the glucose is partially converted to fructose to yield a liquid sweetener known as high fructose corn syrup (HFCS). In plants that can alternate between fuel ethanol and HFCS production, relatively more ethanol is produced in the winter, while relatively more HFCS is produced in the summer.

The gluten product, known as corn gluten meal, contains 60% protein and is used primarily as poultry feed. The fiber from the hulls is combined with

other byproducts, such as the oil cake, steep water solubles, and excess yeast from stillage, dried and sold as corn gluten feed. Containing 21% or more of protein, it is primarily used as feed for dairy cattle.

A typical wet milling plant will produce about 10.6 L (2.8 gal) of ethanol per bushel of corn processed. Yields of other coproducts per bushel of corn are 0.7 kg (1.7 lb) of corn oil, 1.4 kg (3 lb) of corn gluten meal (60% protein), 5.9 kg (13 lb) of corn gluten feed (21% protein), and 7.7 kg (17 lb) of carbon dioxide. Like dry milling, the three products of ethanol, feed, and carbon dioxide are produced in approximately equal weight per bushel, with each accounting for approximately one-third of the initial weight of the corn.

7.2.5 Fermentations to Products Other Than Ethanol

Only a small fraction of commercial production of organic compounds comes from microbial processes. With the exception of ethanol, most fermentation products are specialty chemicals including carboxylic acids, amino acids, antibiotics, industrial and food enzymes, and pharmaceuticals. Examples of organic chemicals produced from fermentation are listed in Table 7.2.

Although many biorenewable resources are cheaper than petroleum, virtually all commodity organic chemicals are produced from petroleum, because processing costs are generally much cheaper for the conversion of hydrocarbons to these products. Only a few fermentation products can be considered as commodity chemicals (worldwide production exceeding 50 000 tons per year): ethanol, monosodium glutamate, citric acid, lysine, and gluconic acid. Ethanol leads this group (15 million tons per year) by virtue of various tax incentives for its manufacture from renewable resources. New developments in fractionation of lignocellulose to simple sugars and environmental considerations may ultimately increase the production of commodity chemicals from biorenewable resources.

Only a relative small number of organic compounds are produced as the primary products of anaerobic fermentation. These include a few simple alcohols and acids, a single ketone (acetone), and two gases of interest as fuel: methane and hydrogen. All of these products are derived from the single intermediate, pyruvate. The primary substrates for most of these fermentations are monosaccharides or oligosaccharides consisting of two or three monosaccharides. Because transport of nutrients and metabolic products through the cell walls of microorganisms are limited to low-molecular-weight compounds, the higher oligosaccharides and polysaccharides must be depolymerized outside the organisms to low-molecular-weight sugars before they can be metabolized. Microorganisms accomplish this by secreting enzymes such as amylase or cellulase to break down starch and cellulose, respectively, to sugars that can be transported into the cell. The following paragraphs describe how various commodity chemicals could be produced through fermentation.

Table 7.2 Examples of chemical products from fermentation of carbohydrates

Chemical	Substrate(s)	Microorganism(s)
Acetic acid	Various sugars	*Acetobacter aceti* *Clostridium thermoaceticum* *Pachysolen tannophilus*
Acetone	Various sugars	*Clostridium* sp.
2,3-Butanediol	Various sugars and acids	*Aerobacter aerogenes* *Bacillus polymyxa* *Klebsiella oxytoca* *Klebsiella pneumoniae*
n-Butanol	Various sugars and organics	*Clostridium* sp.
Butyraldehyde	Glucose	*Clostridium acetobutylicum*
Butyric acid	Various sugars	*Clostridium* sp.
Citric acid	Various sugars	*Aspergillus niger* *Saccharomycopsis lipolytica*
Ethanol	Various sugars	*Kluyveromyces* sp. *Candida utilis* *Saccharomyces cerevisiae* *Zymomonas mobilis*
C12–C20 fatty acids	Sucrose	Bacteria, mold, yeast
Gluconic acid	Glucose	*Aspergillus niger* *Gluconobacter suboxydans*
Isopropyl alcohol	Various sugars	*Clostridium* sp.
Itaconic acid	Glucose, sucrose	*Aspergillus itaconicus* *Ustilago zeae* *Aspergillus terreus*
Linoleic acid	Glucose, lactose	*Candida curvata*
Linolenic acid	Various sugars	*Mortierella ramammiana*
Oleic acid	Glucose, lactose	*Candida curvata*
Palmitic acid	Glucose, lactose	*Candida curvata*
Propanediol	Algal biomass, glucose	*Clostridium pasteurianum* *C. thermosaccharolyticum*
n-Propanol	Glucose	*Clostridium fallax*
Propionic acid	Various sugars	*Clostridium* sp. *Propionibacterium shermanii*
Pyruvic acid	Glucose	*Pseudomonas aeruginosa*
Sorbitol	Sucrose	*Zymomonas* sp.
Stearic acid	Glucose, lactose	*Candida curvata*
Succinic acid	Various sugars	Many species

Source: Leeper, S.A., Ward, T.E., and Andrews, G.F. (1991) Production of organic chemicals via bioconversion: a review of the potential. Report EGG-BG-9033. Idaho Falls, ID: Idaho National Engineering Laboratory.

Butanol

Butanol can be produced biologically through so-called acetone–butanol–ethanol (ABE) fermentation. Certain strains of *Clostridia* bacteria, particularly *Clostridium acetobutylicum* and *Clostridium beijerinckii* are able to ferment soluble C6 and C5 sugars in two distinct phases. The first phase of acidogenesis produces carboxylic acids such as lactic, acetic, and butyric acids and carbon dioxide and hydrogen. In the second phase, solventogenesis converts these acids to solvents including

acetone, butanol, and ethanol. Typical product ratios of acetone, butanol, and ethanol are 3:6:1.

ABE fermentations were used commercially during World War I for production of acetone and in the 1940s and 1950s to produce biobutanol although it was eventually superseded by cheaper petroleum-derived butanol. In batch fermentations, yields are limited by *Clostridia*'s susceptibility to butanol toxicity, which resulted in high cost of butanol recovery from the dilute product solutions. Reactor productivity of butanol is typically limited to 0.5 g/L/h and concentrations of only 20 g/L.

A number of techniques have been recently developed to improve the prospects for butanol fermentation, including introduction of hyper-butanol-producing strains, cell immobilization, continuous fermentation, alternative product recovery techniques. As a result, reactor productivity has increased a factor of 10–30 and concentrations increased a factor of three or more. Fermentation substrates other than sugar are possible. *Clostridium pasteurianum* can convert glycerol into butanol at a maximum concentration of 17.0 g/L. *Clostridium carboxidivorans* P7 is able to ferment syngas from the gasification of biomass although producing butanol at relatively low concentrations (2.2 mg/L), which could be improved by enhancing mass transfer between the syngas and the aqueous fermentation broth (e.g., using hollow membrane fibers).

2,3-Butanediol

The heating value of butanediol (27 198 J/g) is close to that of ethanol (29 055 J/g) and methanol (22 081 J/g), making it a potentially attractive fuel. Many strains of microorganisms are able to ferment five- and six-carbon sugars to 2,3-butanediol including *Bacillus polymyxa* and *Klebsiella (Aerobacter) pneumoniae*. Under anaerobic conditions, approximately equimolar amounts of ethanol and 2,3-butanediol are produced by all strains. Limited aeration decreases ethanol production and 2,3-butanediol becomes the major or even sole product. Final product concentration for *B. polymyxa* is only 2–3% w/v, while *K. pneumoniae* can accumulate to 6–8% w/v. Recovery of 2,3-butanediol is difficult for several reasons, including high boiling point, high heat of vaporization, and its hydrophilic nature.

Aliphatic Acids

Aliphatic acids are derived from straight- or branched-chain organic compounds that include alkenes, alkanes, or alkynes. Some short-chain aliphatic acids, such as acetic and propionic acids, can be produced as major products of fermentation. More typically, though, a mixture of acids and alcohols are produced. These are the same acetogenic bacteria involved in anaerobic digestion as described in Chapter 9 except that the methanogenic step is not allowed to proceed. The accumulating organic acids are toxic to the microorganisms that create them. Hydroxides or carbonates of sodium, potassium, magnesium, calcium, or ammonium are added to

the fermentation broth to neutralize organic acids as they are formed. For example, *Clostridium thermoaceticum* and *Clostridium thermoautotropicum* ferment fructose and a few six-carbon sugars to two moles of acetate by decarboxylation of pyruvate, while the third mole is produced by reduction and incorporation of CO_2.

High base consumption is an inherent feature of organic acid fermentation; the resulting salts of aliphatic acids (acetate) must be decomposed and the cations must be recovered if the process is to be cost-effective. One approach is to pyrolyze the resulting acetate at 300°C to form ketones such as 2-propanone, 2-butanone, 2-pentanone, and 3-pentanone. The mixed ketones, which have high energy content, high octane rating, and boiling range compatible with gasoline, have been proposed as transportation fuel. Alternatively, the ketones can be hydrogenated to mixed alcohols (i.e., 2-propanol, 2-butanol, 2-pentanol, and 3-pentanol).

Lactic Acid

Lactic acid, a three-carbon molecule, is used in the production of polylactide (PLA) resin, a biodegradable polymer expected to compete with polyethylene and polystyrene in the synthetic fibers and plastics markets. Lactic acid is currently produced by milling corn, separating the starch, hydrolyzing the starch to glucose, and anaerobically fermenting the glucose to lactic acid with *Bacillus dextrolacticus* or *Lactobacillus delbrueckii*. Esterification with ethanol produces ethyl lactate, which can be polymerized to polylactate resin.

Succinic Acid

Succinic acid is used in producing food and pharmaceutical products, surfactants and detergents, biodegradable solvents and plastics, and ingredients to stimulate animal and plant growth. Although it is a common metabolite formed by plants, animals, and microorganisms, its current commercial production of 15 000 tons per year is from petroleum. However, the recently discovered rumen organism *Actinobacillus succinogenes* produces succinic acid with yields as high as 110 g/L, offering prospects for producing this chemical from biorenewable resources. In contrast to most other commercial fermentations, the process consumes carbon dioxide; integrated with a process like ethanol fermentation, succinic acid production could contribute toward reductions in greenhouse gas emissions.

Optimum yields occur under pH conditions where succinate salt rather than free acid is produced. Thus, recovery entails concentration of the salt, conversion back to free acid, and polishing of the acid to desired purity. Downstream purification can account for 60–70% of the product cost. One recovery approach uses calcium hydroxide to precipitate calcium succinate from the fermentation broth. Acidification of the precipitate yields gypsum. Disadvantages include handling and disposing of large amounts of wet gypsum. Another recovery approach employs simultaneous electrodialysis, acidification, and crystallization. Sodium succinate

and other ionic species are transported across the ion-exchange membranes and separated from concentrated sugars, proteins, and amino acids.

Hydrocarbons

Hydrocarbons can also be synthesized in microbial fermentations. The common yeast *Saccharomyces* can synthesize a variety of straight-chain and branched-chain hydrocarbons containing between 10 and 34 carbon atoms, which is a range suitable for upgrading to transportation fuels. Yields are a respectable 10.2 wt% of dry biomass under anaerobic conditions. The highest reported yield of hydrocarbons in wild-type bacteria is the salt-tolerant bacterium *Vibrio furnissii*, which produces hydrocarbons at 60 wt% of dry biomass. More commonly, hydrocarbon yields are just a few percent weight of dry biomass. Metabolic engineering could improve yields of hydrocarbons by mapping metabolic fluxes associated with their production and identifying enzymes responsible for hydrocarbon synthesis.

For example, terpene synthesis has been promoted in both eukaryotes and prokaryotes through metabolic engineering. Unlike most biomolecules, which incorporate copious quantities of oxygen into their molecular structures, terpenes contain little or no oxygen. Terpenes are constructed from a molecular building block known as isoprene C_5H_8, which is one of a class of compounds characterized by the presence of two pairs of double carbon bonds separated by a single carbon bond (isoprenes). Both terminal carbon atoms can bond with terminal carbon atoms of other isoprenes to form a variety of hydrocarbon compounds with different degrees of saturation (also of interest are closely related terpenoids, which are derived from terpenes by moving or removing methyl groups or adding oxygen atoms). Like other forms of lipids, terpenes must be upgraded to a final fuel product. Although very little oxygen would have to be removed, saturation and structural rearrangement of the terpene molecules is required to obtain suitable gasoline, diesel fuel, or aviation fuel products.

7.3 Conversion of Lignocellulosic Feedstocks to Sugar

Much of the carbohydrate in plant materials is structural polysaccharides, providing shape and strength to the plant. The hydrolysis of polysaccharides in cell walls is more difficult than the hydrolysis of storage polysaccharides such as starch. This structural material, known as lignocellulose, is a composite of cellulose fibers embedded in a cross-linked lignin–hemicellulose matrix. Depolymerization to basic plant components is difficult, because lignocellulose is resistant to both chemical and biological attack.

A variety of physical, chemical, and enzymatic processes have been developed to fractionate lignocellulose into the major plant components of hemicellulose,

cellulose, and lignin. The hemicellulose fraction is readily hydrolyzed to pentoses (five-carbon sugars), but pentoses are difficult to ferment. The cellulose exists as both amorphous and crystalline forms, which hydrolyze to hexoses (six-carbon sugars). Crystalline cellulose is recalcitrant to hydrolysis. However, the resulting hexoses are readily fermented. Distillation can recover the desired products of fermentation. Lignin, which is not susceptible to biological transformation, can be chemically upgraded or, more frequently, simply burned as boiler fuel. The steps of pretreatment, hydrolysis, fermentation, and distillation in the production of biobased products from lignocellulose are described in the following sections.

7.3.1 Pretreatment

Pretreatment is one of the most costly steps in conversion of lignocellulose to sugars, accounting for about 33% of the total processing costs. Pretreatments often produce biological inhibitors, which impact the cost of fermenting the resulting sugars. Accordingly, much attention is directed at developing low cost and effective pretreatments.

An important goal of all pretreatments is to increase the surface area of lignocellulosic material, making the polysaccharides more susceptible to hydrolysis. Thus, comminution, or size reduction, is an integral part of all pretreatments. Primary size reduction employs hammer mills to produce particles that can pass through 3 mm screen openings. The process has relatively modest energy requirements, ranging from 24 000 kJ per dry ton for wheat straw to 200 000 kJ per dry ton for aspen wood. However, energy consumption increases exponentially with decreasing particle size. If the subsequent hydrolysis process requires further improvements in accessibility and susceptibility of polysaccharides, alternatives to finer milling are usually employed.

As described in the next section, three types of hydrolysis have been developed for releasing sugars from lignocellulose: two that employ mineral acids and one based on enzymes. The molecules of mineral acids, which are small compared to the pore volume of plant tissue, diffuse deeply into lignocellulosic material; thus primary size reduction produces sufficient surface area for acid hydrolysis. Additional pretreatment prior to acid hydrolysis, though, is often practiced to improve the yield of pentose sugars, as subsequently explained. Enzymatic hydrolysis always requires pretreatment beyond size reduction. Cellulase enzymes are large proteins with molecular weights ranging from 30 000 to 60 000 and are thought to be ellipsoidal with major and minor dimensions of 30 and 200 Å. Typically, only 20% of the pore volume of plant tissue is accessible to these large molecules. Without additional pretreatment, sugar yields from enzymatic hydrolysis are less than 20% of theoretical, whereas pretreatment can increase yields to 90% and higher.

The mechanisms by which pretreatments improve the digestibility of lignocellulose are not well understood. Pretreatment effectiveness has been correlated

with removal of hemicellulose and lignin. Lignin solubilization is beneficial for subsequent hydrolysis, but may also produce derivatives that inhibit enzyme activity. Some pretreatments are thought to reduce crystallinity of cellulose, which improves reactivity, but this does not appear to be the key for many successfully pretreatments. The large variety of pretreatment processes developed can be broadly classified as biological, alkaline, steam explosion, prehydrolysis, ammonia fiber explosion (AFEX), and treatment with organic solvents.

Biological pretreatments employ microorganisms that produce lignin-degrading enzymes (ligninase). As lignin is decomposed, cellulose and hemicellulose are released from the lignocellulosic matrix. The exploitation of ligninase-producing microorganisms has been little developed and faces several hurdles including long reaction times (measured in weeks) and the fact that many ligninolytic microorganisms also produce cellulases and hemicellulases and grow on the resulting sugars, degrading yields.

Alkali metal hydroxides not only break lignin–hemicellulose bonds but also dissolve lignin and hemicelluloses. At very high concentrations (5–20 wt%) alkaline metal hydroxides also swell cellulose. The degradative and dissolving action of hot sodium hydroxide solutions is the basis of the kraft pulping process described in Chapter 10. However, alkali pulping creates long cellulose fibers, which complicates subsequent biochemical processing, and destroys hemicelluloses, a significant source of fermentable sugars. The process can be adjusted to provide a pretreatment that is compatible with subsequent enzymatic hydrolysis of herbaceous biomass, such as wheat straw and cornstover, and some hardwoods. It has not been achieved for softwoods. A barrier to commercial use of this pretreatment is the significant amount of chemicals consumed in neutralizing the acidic carboxylic groups in biomass.

Steam explosion involves saturation of the pores of plant materials with steam followed by rapid decompression; the explosive expansion of steam reduces the plant material to separated fibers, presumably increasing the accessibility of polysaccharides to subsequent hydrolysis. Early research focused on the mechanical disruption of plant tissues and employed relatively high temperatures (220–270°C) and short residence times (40–90 s). Conditions and equipment for steam explosion are similar to the commercial masonite process developed in the 1930s for the production of fiberboard.

For sugar production from lignocellulose, recent research suggests that more important than mechanical disruption are chemical changes that occur prior to the rapid decompression step, including hydrolysis of hemicellulose and the condensation of lignin into small droplets. The removal of hemicelluloses and concurrent condensation of lignin creates numerous large pores in hardwoods and herbaceous biomass, which allow penetration of cellulase enzymes to cellulose fibers. Researchers discovered that comparable hydrolysis of hemicellulose could be achieved at lower temperatures (190–210°C) by use of longer residence times

(3–15 minutes), while reducing pyrolytic decomposition. Hydrolysis of hemicellulose yields mostly pentoses. Xylan, the most common polysaccharide in hemicelluloses, consists of xylose units. Thus, the dominant pentose in the hydrolysate from hemicellulose is xylose followed by arabinose.

This steaming of biomass for several minutes is called autohydrolysis based on the hypothesis that acidic compounds released from the biomass are responsible for the process. Although this hypothesis has never been proven, the name persists in the literature. The main drawback of autohydrolysis is the relatively low yield of hemicellulosic sugars (about 50%) due to partial hydrolysis and pyrolytic decomposition at high temperatures. Furthermore, the process is not effective with softwoods.

Addition of small amounts of mineral acid, usually sulfuric acid, improves hydrolysis of hemicellulose at reduced temperatures. This process is variously known as prehydrolysis, dilute acid pretreatment, or acid-catalyzed steam explosion. The comminuted biomass is treated with 1 wt% sulfuric acid and incubated at 140°C for 30 minutes or at 160°C for as little as 5–10 minutes to achieve complete hemicellulose removal, which increases enzymatic digestibility of the remaining cellulose to as high as 90%.

Alternatively, sulfur dioxide gas can be added in the amount of 2–3 wt% to moist biomass chips and heated to 150°C for 20 minutes to hydrolyze hemicellulose. The sulfur dioxide rapidly diffuses into biomass pores before it is converted into sulfuric acid, providing superior performance compared to the direct use of an acid catalyst. It is far less corrosive than mineral acids. Steam pretreatment of hardwoods using SO_2 can recover more than 80% of the hemicellulose as monomers, more than 90% of the lignin by alkali washing, while enzymatic hydrolysis of the pretreated biomass can convert 100% of the cellulose to fermentable sugars. The same process can recover 65% of the hemicellulose as monomers, 80% of the lignin by a combination of both alkali and peroxide washing, and complete conversion of the cellulose by enzymatic hydrolysis. Corncobs, which have very high hemicellulose content, are particularly easy to digest. Prehydrolysis at 150°C converts the hemicellulose to xylose after only 5 minutes.

The resulting prehydrolysates contain soluble dextrins and sugars, acetic acid, furfural, and low-molecular weight phenols derived from lignin, and other fermentation inhibitors. The acetic acid is inhibitory to fermentation above a threshold value of 0.5 g/L. Hardwoods such as aspen release as much as 6–10 g/L of acetic acid during prehydrolysis, while softwoods, which have fewer acetate groups in their hemicellulose, produce 2–4 g/L. Acetic acid and other volatile compounds can be readily removed from the pretreated biomass by steam to the required 0.5 g/L level or less. Furfural and other volatile compounds are also stripped out.

Prehydrolysis also yields furfural from xylose, which can be recovered during the flash cooling that occurs during pressure letdown at the discharge of the reactor. Furfural, which is a valuable solvent in oil refining and is also a base for furan

resins, has been commercially produced from a variety of agricultural residues, including corncobs, cornstover, and oat hulls.

A disadvantage of prehydrolysis is the need to neutralize the acidified biomass. Although calcium hydroxide (lime) is a relatively inexpensive base, the resulting calcium sulfate (gypsum) is of low value and represents a waste disposal problem. Also, some sugar decomposition invariably occurs.

Ammonia fiber explosion is similar to steam explosion except that liquid ammonia is employed. Pressures exceeding 12 atm are required for operation at ambient temperature with ammonia loadings in the range of 1.0–2.5 kg per kg dry biomass. The mixture is incubated for several minutes to up to an hour to enable ammonia to penetrate the lignocellulosic matrix. Hydrolysis yields from AFEX-treated agricultural residues are 80–90% of theoretical, which is superior to that achieved by prehydrolysis. Furthermore, no gypsum byproduct is generated. The process has not been successfully applied to either hardwoods or softwoods.

Organic solvents have been used for pretreatments to remove lignin from biomass. Lignin can adsorb significant amounts of cellulase enzymes employed for enzymatic hydrolysis of cellulose. Thus, lignin removal can decrease the requirement for costly enzymes in downstream processing. Selective removal of lignin can be accomplished by the addition of organic solvents (usually lower alcohols) to the acidic or alkaline aqueous solutions of pulping or pretreatment processes.

7.3.2 Hydrolysis

Three basic methods for hydrolyzing structural polysaccharides in plant cell walls to fermentable sugars are available: concentrated acid hydrolysis, dilute acid hydrolysis, and enzymatic hydrolysis. The two acid processes hydrolyze both hemicellulose and cellulose with very little pretreatment beyond comminution of the lignocellulosic material to particles of about 1 mm size. The enzymatic process must be preceded by extensive pretreatment to separate the cellulose, hemicellulose, and lignin fractions.

Concentrated acid hydrolysis is based on the discovery over a century ago that carbohydrates in wood will dissolve in 72% sulfuric acid at room temperature, leaving behind the lignin fraction. For fermentation, the solution of oligosaccharides is diluted to 4% H_2SO_4 and heated at the boiling point for 4 hours or in an autoclave at 120°C for 1 hour to yield monosaccharides. Following neutralization with limestone, the sugar solution can be fermented. Concentrated acid hydrolysis is relatively simple and is attractive for its high sugar yields, which approach 100% of theoretical hexose yields.

Both sulfuric acid and hydrochloric acid have been considered for commercial development of concentrated acid hydrolysis. The low price of sulfuric acid makes it attractive as a hydrolyzing agent. Nevertheless, the large volume of acid required, about equal to the weight of sugars produced, mandates its recovery and reuse. The

recovery of sulfuric acid is complicated by its high boiling point. Electrodialysis and solvent extraction are possible recovery options. Hydrochloric acid is significantly more expensive and corrosive than sulfuric acid, but its higher volatility presents opportunities for recovery by distillation. Evaporation under vacuum yields a high boiling azeotrope (18% HCl, 120°C), which presents difficulties in further recovery. Neutralization of the acid with limestone also generates a large waste stream of gypsum ($CaSO_4$). An ethanol plant would generate over 2 kg of gypsum per liter of ethanol produced, or 40 000 tons of wet gypsum for a 20 million L/year plant.

Dilute acid hydrolysis (about 1% acid by weight) greatly reduces the amount of acid required to hydrolyze lignocellulose. The process is accelerated by operation at elevated temperatures: 100–160°C for hemicellulose and 180–220°C for cellulose. Unfortunately, the high temperatures cause oligosaccharides released from the lignocellulose to decompose, greatly reducing yields of simple sugars to only 55–60% of the theoretical yield. The decomposition products include a large number of microbial toxins such as acetic acid and furfural, which inhibit fermentation of the sugars. The need for corrosion-resistant equipment and low concentrations of sugars from some reactor systems also adversely impact the cost of sugars.

Early efforts in both concentrated and dilute acid hydrolysis of lignocellulose focused on recovery of hexoses, which are easily fermentable. Pentoses released from hemicellulose were considered of little value and no attempt was made to recover them or prevent their degradation. Since biomass is a relatively expensive feedstock, recovery of both hexoses and pentoses is now considered essential to the economic viability of any lignocellulose-to-sugars process. Toward this end, acid hydrolysis processes have incorporated pretreatments not for the purpose of increasing cellulose accessibility but to separately recover pentose from hemicellulose to prevent its degradation under the harsh conditions of acid hydrolysis.

An example of a lignocellulose-to-ethanol plant based on concentrated acid hydrolysis with pretreatment to recover hemicellulose is illustrated in Figure 7.4. Milled biomass is conveyed to a prehydrolysis (hemicellulose) reactor for the purpose of converting hemicellulose into pentose. The biomass is treated with a stream of 9% sulfuric acid and dissolved glucose is recycled from the concentrated acid (cellulose) reactor. The slurry is heated to 100°C for 2–3 hours, which is sufficient to hydrolyze the hemicellulose. The liquid, containing both pentose and hexose, is pressed from the biomass, neutralized with limestone, filtered to remove the resulting gypsum, and sent to a fermentor. The prehydrolyzed biomass enters one or more stages of a concentrated acid (cellulose) reactor where it is treated with 70% sulfuric acid at 100°C for 2–4 hours. Hydrolysis yields hexose and lignin, which is removed by a filter press. The acidic sugar solution is recycled to the prehydrolysis reactor. When cornstover is used as feedstock, alcohol recovery is 315 L per ton of biomass.

A dilute acid hydrolysis plant with pretreatment to recover hemicellulose is illustrated in Figure 7.5. The process resembles the concentrated acid plant except

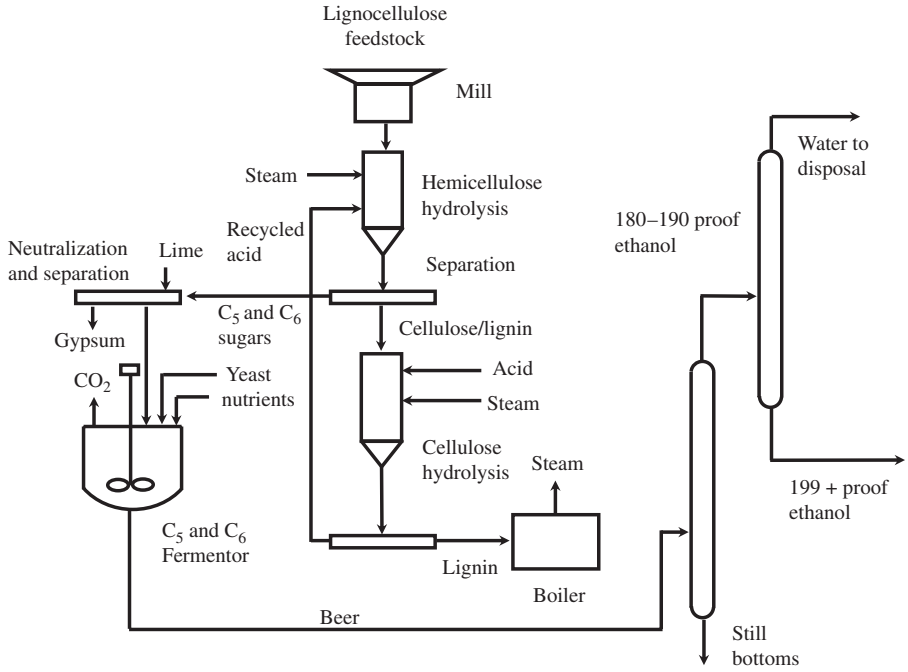

FIG. 7.4 Concentrated acid hydrolysis of lignocellulosic biomass.

that pentoses are recovered and fermented separately from the hexose and cellulose is hydrolyzed with dilute sulfuric acid. Biomass is impregnated with 1% sulfuric acid and heated with saturated steam at 1.24 MPa for 4 minutes to prehydrolyze hemicellulose. The pentoses are separated from the residual lignocellulose by filtering, neutralized with limestone, and sent to a pentose fermentor. The residual lignocellulose is impregnated with 3% sulfuric acid and heated with steam at 2 MPa for 4 minutes to hydrolyze the cellulose. The hexose solution is filtered from the lignin residue, neutralized with limestone, and fermented in a hexose fermentor. The lignin is used as boiler fuel. The yield of alcohol from poplar wood is 250 L per ton.

Enzymatic hydrolysis was developed to better utilize both cellulose and hemicellulose from lignocellulosic materials. Pretreatment solubilizes hemicellulose under milder conditions than those required for acid hydrolysis of cellulose. Subsequent enzymatic hydrolysis of the cellulose does not degrade pentoses released during prehydrolysis.

Cellulose is a homopolysaccharide of glucose linked by β-1,4'-glycosidic bonds. Thus, enzymatic hydrolysis of cellulose proceeds in several steps to break glycosidic bonds by the action of a system of enzymes known as cellulase. Native cellulose is hydrolyzed by the isoenzymes cellobiohydrolase I and cellobiohydrolase II to yield

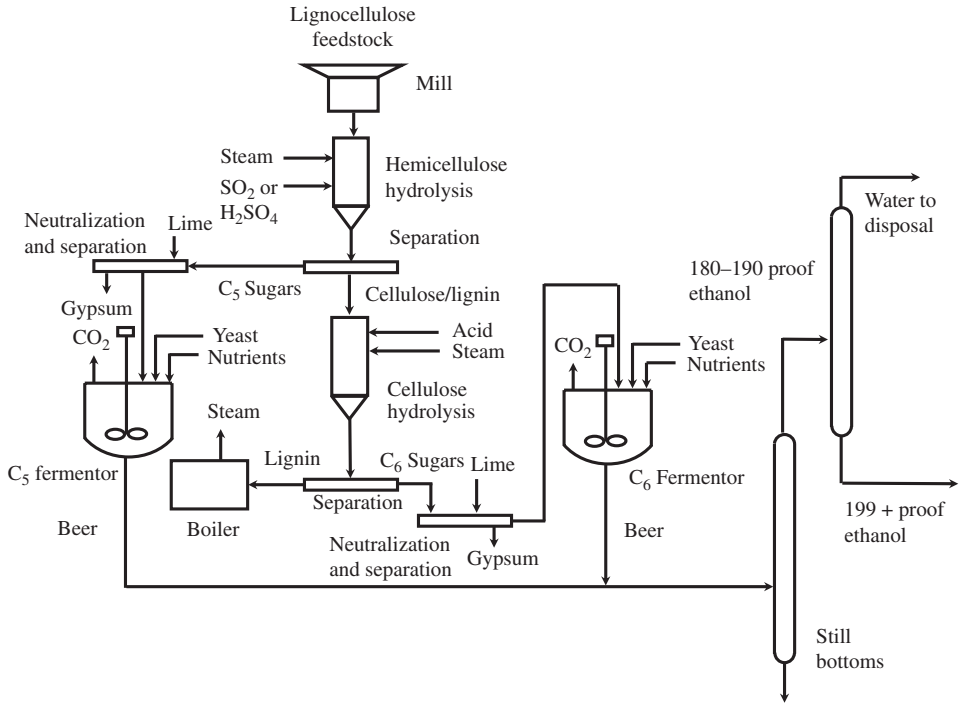

FIG. 7.5 Dilute acid hydrolysis of lignocellulosic biomass.

cellodextrins and cellobiose. The cellodextrins are further hydrolyzed to cellobiose, a disaccharide of glucose, by the isoenzymes endoglucanase I and endoglucanase II. The cellobiose is hydrolyzed to monosaccharide by β-glucosidase. The system of enzymes also usually contains hemicellulase to hydrolyze any hemicellulose not solubilized by prehydrolysis.

A variety of fungi and bacteria produce cellulases both aerobically and anaerobically. The aerobic mesophilic fungus *Trichoderma reesei* and mutants of it have been the most intensely studied sources of cellulases. Other fungal cellulase producers include *Trichoderma viride*, *Trichoderma lignorum*, *Trichoderma koningii*, *Penicillium* spp., *Fusarium* spp., *Aspergillus* spp., *Chrysosporium pannorum*, and *Sclerotium rolfsii*. The problems with enzymatic hydrolysis are relatively low specific activity, low rates of conversion, and sensitivity to end product inhibition. The low specific activity leads to high enzyme loading requirements: approximately 1 kg of enzyme is needed for hydrolysis of 50 kg of cellulose fibers. Conversion rates are as low as 20% in 24 hours; thus, up to 7 days are required to digest lignocellulose. Simultaneously hydrolyzing cellulose and fermenting hexose as it is released, a technique described in the next section, can substantially overcome end product inhibition.

7.3.3 Fermentation

The first step in a successful fermentation is removal of toxic compounds from the hydrolysate that would otherwise inhibit the growth of fermentation organisms. These toxic compounds include furfural and acetic acid, which are breakdown products from hydrolysis of hemicellulose. Traditional detoxification methods, such as the addition of activated carbon, extraction with organic solvents, ion exchange, ion exclusion, molecular sieves, over-liming, and steam stripping, can be costly. Another method under development is adaptation of the fermentation organisms to the inhibitory substances.

Numerous yeast species, including common baker's yeast *S. cerevisiae* and two species of bacteria in the genus *Zymomonas*, efficiently ferment six-carbon sugars to ethanol and carbon dioxide. These microorganisms are suitable for fermenting traditional sugar and starch crops, which yield hexoses upon processing. However, they are not able to ferment the pentoses released from lignocellulosic biomass upon hydrolysis of the hemicellulosic fraction. Efficient conversion of lignocellulosic biomass requires fermentation of pentoses, especially xylose and arabinose.

A variety of microorganisms can directly ferment pentose. Among wild-type yeast genera *Pichia stipitis*, *Candida shehatae*, and *Pachysolen tannophilus* are able to ferment both five-carbon and six-carbon sugars. Maximum yields are on the order of 50 g/L compared to 150 g/L for hexose-fermenting *S. cerevisiae*. A few filamentous fungi, notably within the genera *Fusarium*, *Rhizopus*, and *Paecilomyces*, ferment both five- and six-carbon sugars to ethanol and CO_2, but at low rates and final concentrations of ethanol. Thermophilic bacteria such as *Clostridium thermohydrosulfuricum*, *Clostridium thermosaccharolyticum*, and *Clostridium thermocellum* are able to produce ethanol from both hexoses and pentoses but they have low tolerances for end products. For example, the maximum yield of ethanol by *C. thermocellum* is less than 30 g/L.

Research into using wild-type bacteria and fungi to convert xylose waned during the 1980s, due in part to the widely recognized disadvantages of low rate and/or poor yield of these types of microorganisms, coupled with the fact that moderately productive xylose-fermenting yeasts had been identified. Recombinant DNA techniques are being employed to produce new strains of microorganisms with the desired trait of fermenting both hexoses and pentoses. For example, the bacteria *Escherichia coli* are able to convert both hexoses and pentoses to pyruvate but the end product is acetic acid rather than ethanol. The bacteria *Zymomonas mobilis* are able to convert pyruvate to ethanol but cannot ferment pentose. Using recombinant techniques, researchers transferred pyruvate decarboxylase and alcohol dehydrogenase from *Z. mobilis* to *E. coli*, which resulted in an organism able to ferment up to 90% of the sugars derived from lignocellulose with final ethanol concentrations ranging from 40 to 58 g/L.

Three approaches have been developed for fermenting sugars released from lignocellulose: separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), and CBP.

The SHF process employs separate steps for the unit operations of prehydrolysis, enzymatic hydrolysis, and fermentation. The primary advantage of this approach is that by separating each step, undesirable interactions are avoided. Use of separate reactors for hydrolysis and fermentation allows these two processes to proceed at their optimal temperatures: 50°C for enzymatic hydrolysis and 20–32°C for fermentation. The disadvantage is inhibition of the enzyme β-glucosidase by the hydrolysis product glucose, thus requiring lower solids loadings to obtain reasonable yields. Low sugar concentrations result in lower ethanol concentrations, which increase the cost of fermentation and subsequent product recovery.

The SSF process combines hydrolysis (saccharification) and fermentation to overcome end product inhibition that occurs during hydrolysis of cellobiose. By combining hydrolysis and fermentation in the same reactor, glucose is rapidly removed before it can inhibit further hydrolysis. The SSF process is illustrated in Figure 7.6. Biomass feedstock is milled and then prehydrolyzed to yield a mixture of pentoses, primarily xylose and arabinose, and fiber. The mixture is neutralized with limestone and mixed with cellulase and hemicellulase enzymes, which are either

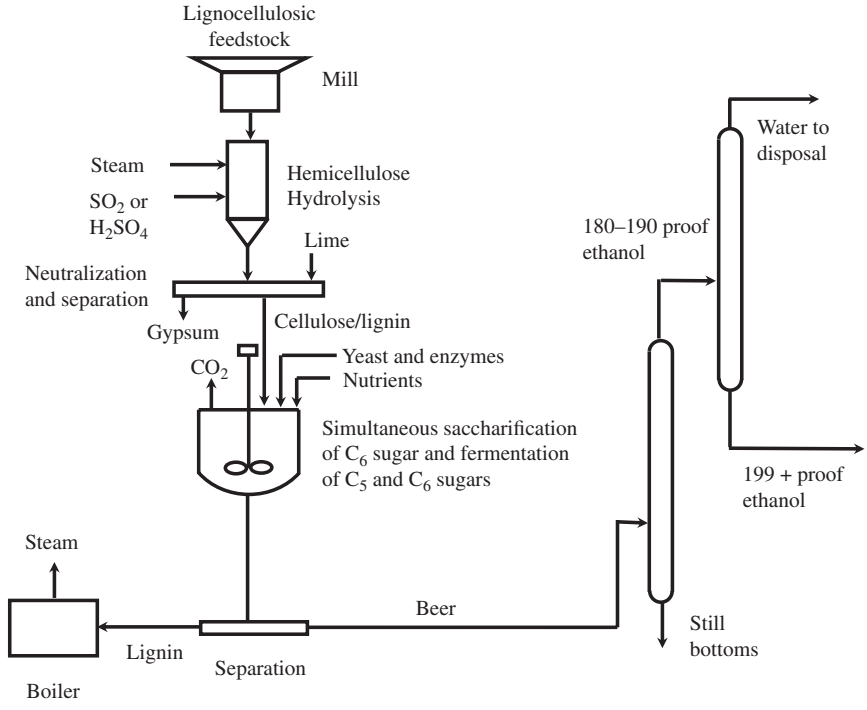

Fig. 7.6 Enzymatic hydrolysis of lignocellulosic biomass.

purchased commercially or produced on site, yeast, and nutrients. The cellulose and any remaining hemicellulose are solubilized to hexose (glucose) and pentoses (xylose and arabinose), which are immediately fermented to ethanol. The rate-limiting step is the hydrolysis of cellulose to glucose. The optimum temperature for the hydrolysis/fermentation reactor is a compromise between the optimum temperature for cellulase activity and the best temperature for the yeast. Lignin is separated from the mixture and used as boiler fuel. The beer is distilled to ethanol in a process identical to that employed after sugar or starch fermentations.

Consolidated bioprocessing, also known as direct microbial conversion (DMC), combines cellulase production, cellulose hydrolysis, and glucose fermentation into a single step. The process is attractive in that it reduces the number of reactors, simplifies operation, and reduces the cost of chemicals. An example of commercially successful application of DMC is anaerobic digestion of sewage sludge and agricultural wastes into methane and carbon dioxide. To date, though, product yields are low, undesired metabolic byproducts are produced, and product inhibition is common. Further development should improve the attractiveness of this approach.

7.4 Distillation

Fermentation can produce gas (such as methane from anaerobic digestion), precipitate (such as calcium acetate during the production of aliphatic acids), or water-soluble compounds (such as ethanol). Gaseous or precipitated products are attractive because of the relative ease of separating them from the spent fermentation broth (beer). Distillation is an energy-intensive process required to recover water-soluble products of fermentation.

The first distillation yields 55% (v/v) ethanol and stillage bottoms, the latter of which contains significant protein in the case of whole-grain fermentation. These stillage bottoms are marketed as animal feed under the name of DDGS. The second distillation produces an ethanol and water azeotrope containing 95–96% ethanol (190–192 proof). If essentially water-free ethanol is desired, purification beyond the azeotrope can be achieved by one of several methods: further distillation in the presence of an entrainer (e.g., benzene, cyclohexane, heptane) that is subsequently recovered; absorption using corn grits or some other solid material; or pervaporation or other membrane-based operation.

Energy consumption in the distillation process is partly responsible for criticism that ethanol production consumes more energy than it produces. Although there is basis for this criticism in older plants, modern plants pay close attention to energy consumption. Some plants are reported to use as little as 5.6 MJ of steam per liter of ethanol produced, with a total energy consumption of 11.1–12.5 MJ/L of product ethanol.

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CHAPTER

8

Thermochemical Processing of Lignocellulosic Biomass

8.1 Introduction

Thermochemical processing uses heat and/or catalysts to convert organic materials into solids, liquids, gases, and/or thermal energy. Four basic thermochemical processes are considered in this chapter: direct combustion, gasification, pyrolysis, and solvolysis. Direct combustion of solid biomass yields hot flue gas that can be used in either the direct-fired or indirect-fired process heaters described in Chapter 6. It can also provide heat to Stirling engines or Rankine steam cycles for the generation of electric power. Gasification yields mostly flammable gases suitable for process heat, power generation, or gaseous and liquid fuel synthesis. Pyrolysis occurs in the absence of oxygen to produce mostly liquid known as bio-oil, which can be used for stationary heat and power applications or upgraded to transportation fuels. It can also be used to depolymerize plant carbohydrates to simple sugars. Solvolysis is the thermal treatment of organic materials in the presence of a solvent. It can be used to extract chemicals, depolymerize and otherwise deconstruct large organic compounds, or even gasify feedstocks.

8.2 Direct Combustion

Combustion is the rapid oxidation of fuel to obtain thermal energy. Because biomass fuels are primarily composed of carbon, hydrogen, and oxygen, the main oxidation products are carbon dioxide and water. Depending on the heating value and moisture content of the fuel, the amount of air used to burn the fuel, and the construction of the furnace, flame temperatures can exceed 1650°C.

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8.2.1 Fundamentals of Combustion

Solid fuel combustion consists of four steps, illustrated in Figure 8.1: heating and drying, pyrolysis, flaming combustion, and char combustion. Heating and drying of the fuel particle is not normally accompanied by chemical reaction. Water is driven from the fuel particle as the thermal front advances into the interior of the particle. As long as water remains, the temperature of the particle cannot increase enough to initiate pyrolysis, the second step in solid fuel combustion.

Pyrolysis is a complicated series of thermally driven chemical reactions that decompose organic compounds in the fuel. Pyrolysis proceeds at relatively low temperatures, which depend on the type of plant material. Hemicellulose begins to pyrolyze at temperatures between 225°C and 325°C and lignin pyrolysis is initiated between 250°C and 500°C.

The resulting decomposition yields a large variety of volatile organic and inorganic compounds, the types and amounts dependent on the fuel and the heating rate of the fuel. Pyrolysis products include carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and high-molecular-weight compounds that condense to a tarry liquid if cooled before they are able to burn. Fine droplets of these condensable compounds represent much of the smoke associated with smoldering fires. Pyrolysis follows the thermal front through the particle, releasing volatile compounds and leaving behind pores that penetrate to the surface of the particle.

Pyrolysis is very rapid compared to the overall burning process and may be as short as a second for small particles of fuel but can extend to many minutes in wood logs. Although the net result of combustion is oxidation of fuel molecules and the release of heat, neither of these processes occurs to a significant extent during pyrolysis. Indeed, if pyrolysis is to proceed at all, heat must be added to the

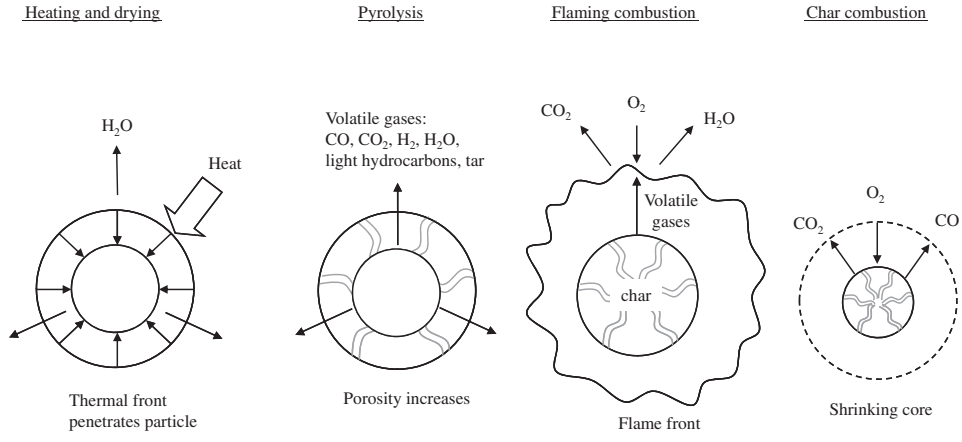

FIG. 8.1 Processes of solid fuel combustion.

fuel. Oxygen is excluded from the pyrolysis zone by the large outflow of gaseous pyrolysis products from the surface of the fuel particle. Only after pyrolysis gases escape the particle and diffuse into the surrounding air are they able to burn. A porous carbonaceous residue known as char remains upon completion of pyrolysis.

Both the volatile gases and the char resulting from pyrolysis can be oxidized if sufficient oxygen is available to them. Oxidation of the volatile gases above the solid fuel results in flaming combustion. The ultimate products of volatile combustion are CO_2 and H_2O although a variety of intermediate chemical compounds can exist in the flame, including CO, condensable organic compounds, and long chains of carbon known as soot. Indeed, hot, glowing soot is responsible for the familiar orange color of wood fires.

Combustion intermediates will be consumed in the flame if sufficient temperature, turbulence, and time are allowed. High combustion temperature assures that chemical reactions will proceed at high rates. Turbulent or vigorous mixing of air with the fuel makes certain that every fuel molecule comes into contact with oxygen molecules. Long residence times for fuel in a combustor allow the fuel to be completely consumed. In the absence of good combustion conditions, a variety of noxious organic compounds can survive the combustion process including CO, soot, polycyclic aromatic hydrocarbons (PAH), and the particularly toxic chlorinated hydrocarbons known as furans and dioxins. In some cases, a poorly operated combustor can produce pollutants from relatively benign fuel molecules.

The next step in combustion of solid fuels is solid–gas reactions of char, also known as glowing combustion, familiar as red-hot embers in a fire. Char is primarily carbon with a small amount of mineral matter interspersed. Char oxidation is controlled by mass transfer of oxygen to the char surface rather than by chemical kinetics, which is very fast at the elevated temperatures of combustion. Depending on the porosity and reactivity of the char and the combustion temperature, oxygen may react with char at the surface of the particle or it may penetrate into the pores before oxidizing char inside the particle. The former situation results in a steadily shrinking core of char, whereas the latter situation produces a constant diameter particle of increasing porosity. Both CO and CO_2 can form at or near the surface of burning char:

$$C + \frac{1}{2}O_2 \rightarrow CO \tag{8.1}$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \tag{8.2}$$

These gases escape the immediate vicinity of the char particle where CO is oxidized to CO_2 if sufficient oxygen and temperature are available; otherwise, it appears in the flue gas as a pollutant.

8.2.2 Combustion Equipment

A combustor is a device that converts the chemical energy of fuels into high-temperature exhaust gases. Heat from the high-temperature gases can be employed in a variety of applications, including space heating, drying, and power generation. However, with the exception of kilns used by the cement industry, most solid fuel combustors today are designed to produce either low-pressure steam for process heat or high-pressure steam for power generation. Combustors integrated with steam-raising equipment are called boilers. In some boiler designs, distinct sections exist for combustion, high-temperature heat transfer, and moderate-temperature heat transfer: these are called the furnace, radiative, and convective sections of the boiler, respectively. In other designs, no clear separation between the processes of combustion and heat transfer exists.

Solid fuel combustors, illustrated in Figure 8.2, can generally be categorized as grate-fired systems, suspension burners, or fluidized beds. Grate-fired systems were the first burner systems to be developed, evolving during the late nineteenth and early twentieth centuries into a variety of automated systems. The most common system is the spreader stoker, consisting of a fuel feeder that mechanically or pneumatically flings fuel onto a moving grate where the fuel burns. Much of the ash falls off the end of the moving grate although some fly

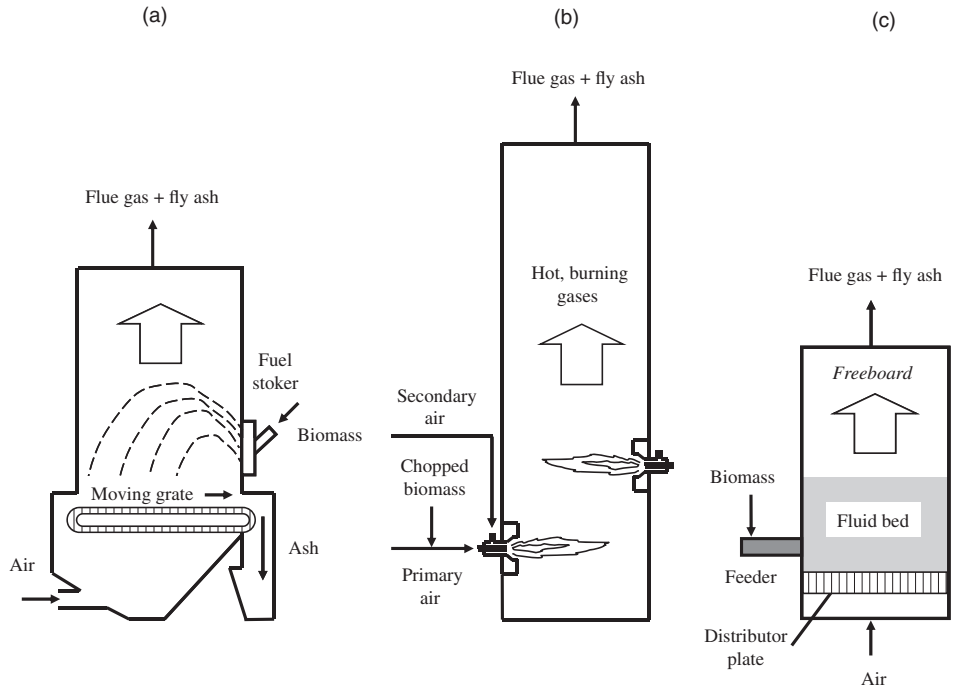

FIG. 8.2 Common types of combustors: (a) grate-fired; (b) suspension; (c) fluidized bed.

ash appears in the flue gas. Grate systems rarely achieve combustion efficiencies exceeding 90%.

Suspension burners were introduced in the 1920s as a means of efficiently burning large quantities of coal pulverized to less than 50 μm particle sizes. Suspension burners suspend the fuel as fine powder in a stream of vertically rising air. The fuel burns in a fireball and radiates heat to tubes that contain water to be converted into steam. Suspension burners, also known as pulverized coal (PC) boilers, have dominated the US power industry since World War II because of their high volumetric heat release rates and their ability to achieve combustion efficiencies, often exceeding 99%. However, they are not well suited to burning coarse particles of biomass fuel and they are notorious generators of nitrogen oxides. Biomass is fed from a bunker through pulverizers designed to reduce fuel particle size enough to burn in suspension. The fuel particles are suspended in the primary airflow and fed to the furnace section of the boiler through burner ports where it burns as a rising fireball. Secondary air injected into the boiler helps complete the combustion process. Heat is absorbed by steam tubes arrayed in banks of heat exchangers (waterwall, superheaters, and economizer) before exiting through a bag house designed to capture ash released from the fuel. Steam produced in the boiler is part of a Rankine power cycle.

Fluidized bed combustors are a recent innovation in boiler design. Air injected into the bottom of the boiler suspends a bed of sand or other granular refractory material producing a turbulent mixture of air and sand. The high rates of heat and mass transfer in this environment are ideal for efficiently burning a variety of fuels. The large thermal mass of the sand bed allows the unit to be operated as low as 850°C, which lowers the emission of nitrogen compounds. A commercial market for fluidized bed boilers was developed during the 1980s, especially for industrial applications.

A whole-tree burner has been proposed for electrical utility steam raising. The advantage of this approach is minimization of field processing and handling and the elimination of fuel chipping, which can save about 35% of the cost of harvesting and handling woody fuels.

A variety of biomass materials have proven suitable for direct combustion, including whole trees, wood chips, forestry residue, agricultural residue, pulp and paper refuse, food processing wastes, municipal solid waste, and straws and grasses. Wood and wood wastes dominate the biomass-to-power market in the United States and much of the rest of the world. Power plants in California have direct-fired agricultural wastes, and Denmark has a number of commercial plants that burn straw.

Direct combustion has the advantage that it employs commercially well-developed technology. There are a number of vendors who supply turnkey systems and considerable operating experience exists both in the United States and abroad. However, there are three prominent disadvantages with direct firing. These

include penalties associated with burning high-moisture fuels, agglomeration and ash fouling due to alkali compounds in biomass, and relatively low thermodynamic efficiencies for steam power plants of the size appropriate to biomass power.

The moisture in biomass degrades boiler performance for two reasons. First, the energy required to vaporize fuel moisture can only be recovered if exhaust gases are cooled sufficiently to condense the water vapor in this gas. Although this procedure would result in very high thermal efficiencies for a boiler burning even very high-moisture fuels, it is not commonly done in practice because the condensate is often corrosive to boiler tubes. Accordingly, most direct-combustion systems are penalized by moisture in the fuel. Second, high-moisture fuels simply do not burn well because the process of fuel drying suppresses fuel temperatures below that required for ignition. Water contents exceeding 30% are unacceptable in most boilers for this reason. Fluidized bed combustors, however, because of the enormous thermal mass associated with the hot bed material, can accept biomass with moisture content as high as 50% although even fluidized beds are penalized in thermal efficiency by the presence of this moisture. Depending on moisture content, as much as 15% of the heating value of biomass is required to dry the fuel. Obviously, field drying of biomass is desired to reduce both transportation costs and heating penalties within the boiler.

Alkali in biomass fuels presents a difficult problem for direct combustion systems. Compounds of alkali metals, such as potassium and sodium salts, are common in rapidly growing plant tissues. Annual biomass crops contain large quantities of alkali, while the old-growth parts of perennial biomass contain relatively small quantities of alkali. These alkali compounds appear as oxides in the residue left after combustion of volatiles and char. Alkali vapors may combine with sulfur and silica to form low-melting-point compounds. These sticky compounds bind ash particles to fuel grates and heat exchanger surfaces. Boiler performance degrades as airflow and heat transfer are restricted by ash deposits. Boilers that fire straw, which contain both high silica and alkali, have experienced serious problems in slagging and fouling as well as high-temperature corrosion unless steam temperatures are kept relatively low (less than 500°C).

As an alternative to completely replacing coal with biomass fuel in a boiler, mixtures of biomass and coal can be burned together in a process known as cofiring. Cofiring offers several advantages for industrial boilers. Industries that generate large quantities of biomass wastes, such as lumber mills or pulp and paper companies, can use cofiring as an alternative to costly landfilling of wastes. Federal regulations also make cofiring attractive. The New Source Performance Standards, which limits particulate emissions from large coal-fired industrial boilers to 0.05 lb/MMBtu, doubles this allowance in cofired boilers in which the capacity factor for biomass exceeds 10%. Adopting cofiring is a good option for companies that are slightly out of compliance with their coal-fired boilers. Similarly, a relatively inexpensive method for a company to reduce sulfur emissions from its boilers is to

cofire with biomass, which contains much less sulfur than coal. Cofiring capability also provides fuel flexibility and reduces ash fouling problems associated with using only biomass as fuel.

The principal disadvantages of cofiring relate to the characteristics of biomass fuels. Because of the lower energy density and higher moisture content of biomass, the steam-generating capacity of cofired boilers is often reduced. Also, the elemental composition of fly ash from biomass is distinct from that of coal fly ash. Utilities are concerned that comingled biomass and coal ash will not meet the American Society for Testing and Materials (ASTM) definition of fly ash that is acceptable for concrete admixtures, thus eliminating an important market for this combustion byproduct.

It is generally recommended that total fuel (single or mix) alkali content be limited to less than 0.17–0.34 kg/GJ (0.4–0.8 lb/MMBtu), which translates to only 5–15% cofiring of biomass with coal. Also, furnace temperatures should be kept below 980°C to help prevent the buildup of alkali-containing mineral combinations known as eutectics. At higher temperatures, molten eutectics bind dirt and other particulates to form slag and fouling deposits.

The best wood-fired power plants, which are typically 20–100 MW in capacity, have heat rates exceeding 12 500 Btu/kWh. In contrast, large, coal-fired power plants have heat rates of only 10 250 Btu/kWh. The relatively low thermodynamic efficiency of steam power plants at the sizes of relevance to biomass power systems may ultimately limit the use of direct combustion to convert biomass fuels to useful energy.

8.3 Gasification

Gasification is the conversion of solid, carbon-rich materials under oxygen-starved conditions and elevated temperatures (typically 750–1500°C) into flammable gas mixtures consisting of carbon monoxide (CO), hydrogen (H_2), methane (CH_4), nitrogen (N_2), carbon dioxide (CO_2), and smaller quantities of higher hydrocarbons and inorganic contaminants like hydrogen sulfide (H_2S) and ammonia (NH_3). The gas mixture is sometimes called syngas (short for synthesis gas), but the raw gas is more properly referred to as producer gas until it has been cleaned and conditioned for use in chemical synthesis.

The release of volatiles from solid fuel is endothermic and requires either the simultaneous burning of part of the fuel or the delivery of an external source of heat to drive the process. Gasification should not be confused with anaerobic digestion, the microbial degradation of biomass to a flammable gas mixture of mostly CH_4 and N_2, a process described in Chapter 9.

Gasification was placed into commercial practice as early as 1812 when coal was converted to gas for illumination (known as manufactured gas or town gas) in

England. This technology was widely adopted in industrialized nations and was employed in the United States as late as the 1950s when interstate pipelines made inexpensive supplies of natural gas available. Some places, such as China and South Africa, still manufacture gas from coal.

The high volatile content of biomass (70–90 wt%) compared to coal (typically 30–40 wt%) and the high reactivity of its char make biomass an ideal gasification feedstock. However, issues of cost and convenience of biomass gasification have limited its applications to special situations and niche markets. For example, in response to petroleum shortages during World War II, over one million small-scale wood gasifiers were built to supply low-enthalpy gas for automobiles and steam boilers. These were abandoned soon after the war.

Not only can producer gas be used for generation of heat and power but also can serve as feedstock for production of liquid fuels and chemicals. Because of this flexibility of application, gasification has been proposed as the basis for "energy refineries" that would provide a variety of energy and chemical products, including electricity and transportation fuels.

8.3.1 Fundamentals of Gasification

Figure 8.3 illustrates the several steps of gasification: heating and drying, pyrolysis, solid–gas reactions that consume char, and gas-phase reactions that adjust the final chemical composition of the producer gas. Drying and pyrolysis are similar to the corresponding processes for direct combustion described in the previous section. Pyrolysis begins between 300°C and 400°C and produces the intermediate products of char: gases (mainly CO, CO_2, H_2, and light hydrocarbons) and condensable vapor (including water, methanol, acetic acid, acetone, and heavy hydrocarbons). The distribution of these products depends on chemical composition of the fuel, the heating rate, and the temperature achieved in the reactor. However, the total pyrolysis yield of pyrolysis products and the amount of char residue can be roughly

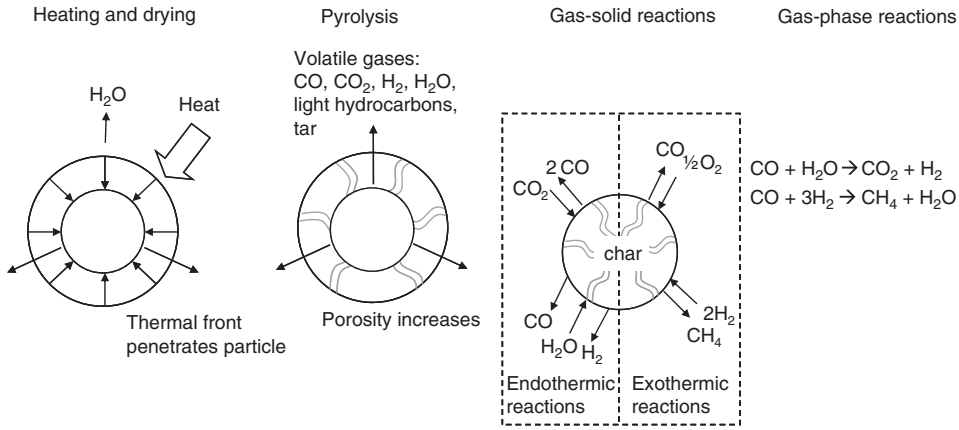

FIG. 8.3 Processes of thermal gasification.

estimated from the proximate analysis of the fuel. The fuel's volatile matter roughly corresponds to the pyrolysis yield while the combination of fixed carbon and ash content can be used to estimate the char yield.

Heating and drying are endothermic processes, requiring a source of heat to drive them. This heat can be supplied by an external source in a process called indirectly heated gasification. More typically, a small amount of air or oxygen (typically not more than 25% of the stoichiometric requirement for complete combustion of the fuel) is admitted for the purpose of partial oxidation, which releases sufficient heat for drying and pyrolysis as well as for the subsequent endothermic chemical reactions described below.

The third step of gasification is gas–solid reactions. These reactions convert solid carbon into gaseous CO, H_2, and CH_4:

$$\text{Carbon–oxygen reaction: } C + \frac{1}{2}O_2 \leftrightarrow CO \quad \Delta H_R = -110.5 \text{ MJ/kmol} \tag{8.3}$$

$$\text{Boudouard reaction: } C + CO_2 \leftrightarrow 2CO \quad \Delta H_R = 172.4 \text{ MJ/kmol} \tag{8.4}$$

$$\text{Carbon–water reaction: } C + H_2O \leftrightarrow H_2 + CO \quad \Delta H_R = 131.3 \text{ MJ/kmol} \tag{8.5}$$

$$\text{Hydrogenation reaction: } C + 2H_2 \leftrightarrow CH_4 \quad \Delta H_R = -74.8 \text{ MJ/kmol} \tag{8.6}$$

The first of these, known as the carbon–oxygen reaction, is strongly exothermic and is important in supplying the energy requirements for drying, pyrolysis, and endothermic solid–gas reactions. The hydrogenation reaction also contributes to the energy requirements of the gasifier, although significantly more char reacts with oxygen than hydrogen in the typical air-blown gasifier.

The fourth step of gasification is gas-phase reactions, which determine the final mix of gaseous products:

$$\text{Water–as shift reaction: } CO + H_2O \leftrightarrow H_2 + CO_2 \quad \Delta H_R = -41.1 \text{ MJ/kmol} \tag{8.7}$$

$$\text{Methanation: } CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \Delta H_R = -206.1 \text{ MJ/kmol} \tag{8.8}$$

The final gas composition is strongly dependent on the amount of oxygen and steam admitted to the reactor as well as the time and temperature of reaction. For sufficiently long reaction times, chemical equilibrium is attained and the products are essentially limited to the light gases CO, CO_2, H_2, and CH_4 (and nitrogen if air was used as a source of oxygen). Analysis of the chemical thermodynamics of these six gasification reactions reveals that low temperatures and high pressures favor the formation of CH_4, whereas high temperatures and low pressures favor the formation of H2 and CO.

Often gasifier temperatures and reaction times are not sufficient to attain chemical equilibrium, and the producer gas contains various amounts of light hydrocarbons such as C_2H_2 and C_2H_4 as well as up to 10 wt% heavy hydrocarbons that condense to form a black, viscous liquid known as "tar." This latter product is undesirable as it can block valves and filters and interferes with downstream conversion processes. Steam injection and addition of catalysts to the reactor are sometimes used to shift products toward lower-molecular-weight compounds.

8.3.2 Gasification Systems

Gasifiers are generally classified according to the method of contacting fuel and gas. The four main types of interest to biomass gasification are updraft (countercurrent), downdraft (concurrent), fluidized bed, and entrained flow. These are illustrated in Figure 8.4, and their performance characteristics are summarized in Table 8.1.

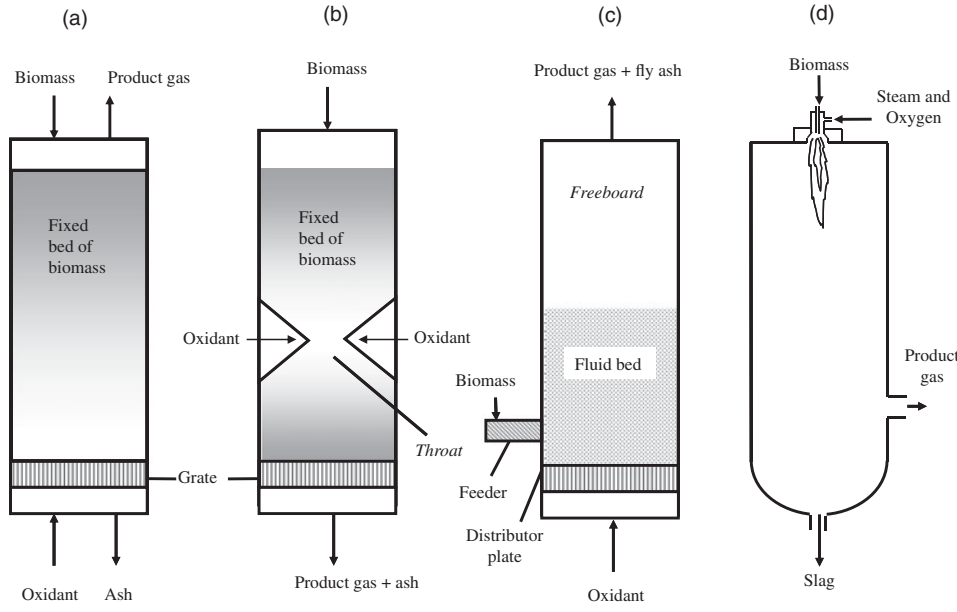

FIG. 8.4 Common types of biomass gasifiers: (a) updraft; (b) downdraft; (c) fluidized bed; (d) entrained flow.

Table 8.1 Producer gas composition from various kinds of gasifiers

	Gaseous Constituents (vol% dry)						Gas Quality	
Gasifier Type	H_2	CO	CO_2	CH_4	N_2	HHV (MJ/m^3)	Tars	Dust
Air-blown updraft	11	24	9	3	53	5.5	High (~50 g/m^3)	Low
Air-blown downdraft	17	21	13	1	48	5.7	Low (~1 g/m^3)	Medium
Air-blown fluidized bed	9	14	20	7	50	5.4	Medium (~10 g/m^3)	High
Oxygen-blown downdraft	32	48	15	2	3	10.4	Low (~1 g/m^3)	Low
Indirectly heated fluidized bed	31	48	0	21	0	17.4	Medium (~10 g/m^3)	High

Source: Bridgwater, A.V. (1995) The technical and economic feasibility of biomass gasification for power generation. *Fuel*, 74, 631—653; Milne, T.A., Abatzoglou, N., and Evans, R.J. (1998) Biomass gasifier "Tars": their nature, formation, and conversion. National Renewable Energy Laboratory Report, NREL/TP-570-25357.

Updraft gasifiers, illustrated in Figure 8.4a, are the simplest as well as the first type of gasifier developed. They were a natural evolution from charcoal kilns, which yield smoky yet flammable gas as a waste product, and blast furnaces, which generate product gas that reduces ore to metallic iron. Updraft gasifiers are little more than grate furnaces with chipped fuel admitted from above and insufficient air for complete combustion entering from below. Above the grate, where air first contacts the fuel, combustion occurs and very high temperatures are produced. Although the gas flow is depleted of oxygen higher in the fuel bed, hot H_2O and CO_2 from combustion near the grate reduce char to H_2 and CO. These reactions cool the gas, but temperatures are still high enough to heat, dry, and pyrolyze the fuel moving down toward the grate. Of course, pyrolysis releases both condensable and noncondensable gases, and the producer gas leaving an updraft gasifier contains large quantities of tars, on the order of 50 g/m^3. As a result, updraft gasifiers are generally not strong candidates for biomass energy applications.

In downdraft gasifiers, fuel and gas move in the same direction. Downdraft gasifiers appear to have been developed near the end of the nineteenth century after the introduction of induced draft fans, which allowed air to be drawn downward through a gasifier in the same direction as the gravity-fed fuel. As shown in Figure 8.4b, contemporary designs usually add an arrangement of tuyeres that admit air or oxygen directly into a region known as the throat where combustion forms a bed of hot char. This design assures that condensable gases released during pyrolysis are forced to flow through the hot char bed, where tars are cracked. The producer gas is relatively free of tar (less than 1 g/m^3), making it a satisfactory fuel for engines. A disadvantage is the need for tightly controlled fuel properties (particles sized to between 1 and 30 cm, low ash content, and moisture less than

30%). Another disadvantage is a tendency for slagging or sintering of ash in the concentrated oxidation zone. Rotating ash grates or similar mechanisms can solve this problem. Furthermore, incorporation of a throat region limits the maximum size of downdraft gasifiers to about 400 kg/h.

In a fluidized bed gasifier, illustrated in Figure 8.4c, a gas stream passes vertically upward through a bed of inert particulate material to form a turbulent mixture of gas and solid. Fuel is added at such a rate that it is only a few percent by weight of the bed inventory. Unlike the updraft and downdraft gasifiers, no segregated regions of combustion, pyrolysis, and tar cracking exist. The violent stirring action makes the bed uniform in temperature and composition, with the result that gasification occurs simultaneously at all locations in the bed. Typically a fluidized gasifier operates in the range of 700–850°C. By injecting fuel in the base of the bed, much of the tar can be cracked within the fluidized bed. However, a large insulated space above the bed, known as the freeboard, is usually included to promote additional tar cracking as well as more complete conversion of char. Nevertheless, tar production is intermediate between updraft and downdraft gasifiers (about 10 g/m^3). Fluidized beds are attractive for biomass gasification. They are able to process a wide variety of fuels including those of high moisture and small size. They are easily scaled to large sizes suitable for electric power production. Disadvantages include relatively high power consumption to move gas through the fluidized bed; high exit gas temperatures, which complicate efficient energy recovery; and relatively high particulate burdens in the gas due to the abrasive forces acting within the fluidized bed.

An entrained flow gasifier, illustrated in Figure 8.4d, injects powdered fuel into a gas flow. Entrained flow reactors are ideal for steam–oxygen gasification of coal at temperatures of 1200–1500°C. If the fuel is finely powdered, these high temperatures assure excellent carbon conversion (approaching 100%) and low tar production even for the short residence times (a few seconds) characteristic of entrained flow gasifiers. The technology is attractive for solid fuels like coal or coke that are easily pulverized, but their use is problematic for biomass, which tends to shred into fibers rather than break into fine powders. Furthermore, the low energy density and high sintering potential of biomass make it difficult to achieve the high temperatures characteristic of entrained flow gasifiers. The high carbon conversion efficiency of entrained flow gasifiers has encouraged researchers to explore ways to utilize biomass feedstocks with them.

One approach, known as torrefaction, slowly heats the biomass in the absence of oxygen at temperatures in the range of 200–350°C. Torrefaction is accompanied by small losses in mass and energy compared to the raw biomass. Torrefied biomass is both more brittle and less hydroscopic than raw biomass, allowing it to be pulverized and mixed with water to produce a slurry suitable for injection into an entrained flow gasifier.

Another approach, known as fast pyrolysis, rapidly heats biomass to temperatures between 350°C and 550°C for the purpose of converting as much as 70 wt% of the biomass into a liquid known as bio-oil and charcoal known as biochar. The bio-oil or a slurry of bio-oil and biochar can be injected under high pressure into an entrained flow gasifier to form a fine spray of liquid droplets that are rapidly gasified.

The fuel:air ratio is the single most important parameter for determining gasifier performance. The conversion efficiency and gas quality of downdraft gasifiers can be superior to fluidized bed gasifiers because they utilize higher fuel/air ratios. Fluidized bed gasifiers, on the other hand, can generally handle a wider range of biomass feedstocks with higher moisture content.

Recent research in biomass gasification has focused on improving the heating value of product gas. Conventional gasification admits sufficient air or oxygen to the reactor to burn part of the fuel thus releasing heat to support pyrolysis of the rest of the fuel. Gas produced in air-blown biomass gasifiers typically has heating value that is only 10–20% that of natural gas. This low heating value is largely the result of nitrogen diluting the fuel gas. Oxygen can be used as the fluidization agent, but high capital costs preclude this from consideration for small-scale energy systems.

Indirectly heated gasification can improve gas heating value by physically separating combustion and pyrolysis. As a result, the products of combustion do not appear in the fuel gas. Higher heating values of 14 200 kJ/m^3 or higher are expected. Several schemes have been suggested for transporting heat from the combustion reactor to the pyrolysis reactor. These include transferring hot solids from the combustor to the pyrolyzer, transferring a chemically regenerative heat carrier between two reactors, transferring heat through a wall common to the reactors, and storing heat in high-temperature phase-change material.

The thermodynamic efficiency of gasifiers is strongly dependent on the kind of gasifier and how the product gas is employed. Some high-temperature, high-pressure gasifiers are able to convert 90% of the chemical energy of solid fuels into chemical and sensible heat of the product gas. However, these high efficiencies come at high capital and operating costs. Most biomass gasifiers have conversion efficiencies ranging between 70% and 80%. In some applications, such as process heaters or driers, both the chemical and sensible heat of the product gas can be utilized. In many power applications, though, the hot product gas must be cooled before it is utilized; thus, the sensible heat of the gas is lost. In this case, "cold gas" efficiency can be as low as 50–60%. Whether the heat removed from the product gas can be recovered for other applications, like steam raising or fuel drying, ultimately determines which of these conversion efficiencies is most meaningful. Gas cleaning to remove tar and particulate matter also has a small negative impact on gasifier efficiency since it removes flammable constituents from the gas (tar and char particles) and generally requires a small amount of energy to run pumps.

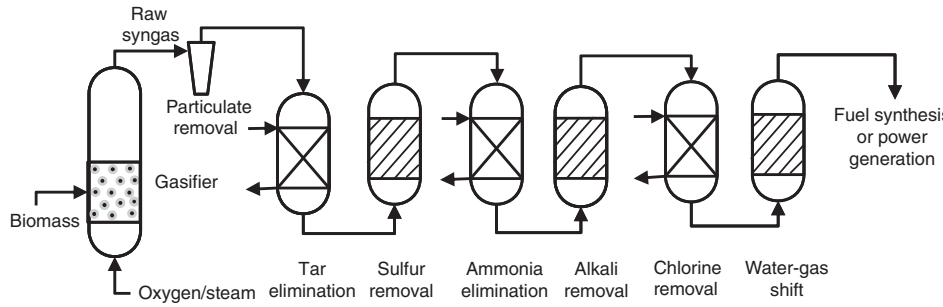

FIG. 8.5 Gas cleaning and conditioning before fuel synthesis or power generation may include several stages, including tar elimination, sulfur removal, ammonia elimination, alkali and chlorine removal, and water–gas shift reaction.

8.3.3 Gas Conditioning

Flammable gas mixtures, whether derived from producer gas, anaerobic digesters, or natural gas, are generally not directly usable as fuel gas or chemical feedstock without some degree of gas conditioning. Gas conditioning includes gas cleaning to remove contaminants and gas enrichment of certain chemical constituents, especially hydrogen (see Figure 8.5). Gas streams from biomass gasification almost always require some level of gas cleaning to meet limits on contaminants in power and fuel synthesis applications. Contaminants to be managed include particulate matter, tar, sulfur, nitrogen, alkali metals, and chlorine (contaminant limits for fuel cell applications are found in Table 6.1, while Table 8.2 contains limits for other applications). Often each type of contaminant requires a separate unit operation to remove or eliminate it from the gas stream although sometimes a single operation is effective against multiple contaminants.

Particulate matter is divided solids, usually in the size range of 0.1–100 μm, suspended in the gas stream. In the case of producer gas, it is primarily mineral

Table 8.2 Gas cleaning levels for producer gas required for select power and fuel synthesis applications

	Application			
Contaminant	IC Engine	Gas Turbine	Methanol Synthesis	FT Synthesis
Particulate	<50 mg/m^3	<30 mg/m^3	<0.02 mg/m^3	Not detectable
Tars	<100 mg/m^3	<8 mg/m^3	<0.1 mg/m^3	<10 ppb
Sulfur	–	<20 ppm	<1 mg/m^3	<10 ppb
Nitrogen	–	<50 ppm	<0.1 mg/m^3	<20 ppb
Alkali	–	<24 ppb	–	<10 ppb
Chloride	–	<1 ppm	<0.1 mg/m^3	<10 ppb

Source: Woolcock, P. and Brown, R.C. (2013) A review of cleaning technologies for biomass-derived syngas. *Biomass and Bioenergy*, 52, 54–84.

matter (ash) and unburned elemental carbon (char) released from gasifying biomass although it may also include inorganic compounds originating from minerals like sand or limestone, which are sometimes added to gasifiers to control their operation. It should be noted that coarser particulate matter may fall to the bottom of a gasifier, in which case it is called bottom ash (although it also contains char) and in very high temperature gasifiers, much of the particulate matter melts and leaves the bottom of the gasifier as molten slag.

Particulate matter is usually the first contaminant to be removed from producer gas because it can interfere with subsequent unit operations. Problems include clogging pipes and orifices and coating heat transfer and chemical catalyst surfaces (ash fouling). The particulate matter also can transport sulfur and nitrogen species that poison catalysts. Particulate matter is removed immediately downstream of the gasifier by gas cyclones operated at temperatures high enough to avoid condensation of tarry compounds in the gas. Cyclones can be very effective down to particulate sizes of about 10 μm, but finer particles are not substantially removed. Because of the high temperatures involved, additional filtration of the finest particles requires ceramic or metal alloy barrier filters or moving bed granular filters.

Tar is any organic compound that condenses from producer gas when it is cooled to room temperature. In appearance, it is a dark, viscous liquid. Tar consists of organic compounds ranging from light oxygenated compounds to PAH. A well-designed gasifier has a high-temperature zone through which pyrolysis products pass, allowing tars to thermally decompose ("crack") into the low-molecular gases predicted by equilibrium theory. Although increasing residence times and temperatures reduce tar yields, those compounds that remain are refractory to further decomposition. Almost all gasifiers produce some level of tar in the product gas stream.

Tar cannot be tolerated in many downstream applications, including internal combustion engines, fuel cells, and chemical synthesis reactors. Tar can deposit on surfaces in filters, heat exchangers, and engines where they reduce component performance and increase maintenance requirements.

Tar can be eliminated from producer gas by either of two methods. One method reacts the gas stream with steam at high temperature to convert the tar to CO and H_2. This "cracking" of tar can be accomplished by raising the gas temperatures above 1000°C. Such high temperatures are not easily achieved in most biomass gasifiers. The use of catalysts, either in the gasifier or immediately after removal of particulate matter, allows tar cracking to occur at much lower temperatures, in the range of 600–800°C. Although catalytic cracking is effective in reducing tar to low levels, the catalysts are susceptible to fouling by the deposition of coke, a tar cracking byproduct, and poisoning by inorganic contaminants in the gas stream.

A simpler approach to gas cleaning scrubs the gas stream with water or oil, which is effective in removing both tar and particulate matter from the gas. The scrubbing liquid is either sprayed countercurrently into the gas stream as a fine mist

or flowed downward by gravity over packing materials in a gas scrubbing column through which the gas flows upward. In either case, the scrubbing liquid both cools the gas, causing the tar to condense as aerosol droplets, and intercepts both solid particles of char and liquid droplets of tar, removing them from the gas flow. The tar and particulate-laden scrubbing liquid exits the scrubbing column for cooling and separation of the contaminants in a settling tank before being reinjected into the dirty gas stream. Because tar contributes to the chemical enthalpy of the producer gas, its removal reduces the overall efficiency of the gasification process (as compared to tar cracking, which recovers the chemical enthalpy of the tar). In fact, the tar recovered by scrubbing becomes a waste disposal problem unless it can be recycled to the gasifier and cracked there. Scrubbing the gas stream with water also produces water contaminated with tar, which requires an additional unit operation of wastewater treatment.

Sulfur appears in producer gas mostly as hydrogen sulfide (H_2S) with lesser amounts of carbonyl sulfide (COS). Although biomass contains significantly less sulfur than coal, it is often high enough to poison many catalysts used to upgrade producer gas to fuel. In some instances sulfur may be limited to a few parts per billion levels (see Table 8.2).

Several gas cleaning technologies have been developed to remove sulfur and other acid gases such as hydrogen chloride. These include both dry- and liquid-based processes operating at a temperature range from subzero to several hundred degrees Celsius. Attempts to remove contaminants at high temperatures (hot gas cleaning) focus on the use of dry sorbents. The challenge is reducing sulfur concentration in the gas stream to as little as a 10 parts per billion.

Most nitrogen from biomass gasification is derived from the thermal decomposition of protein. If chemical equilibrium was achieved during gasification, virtually all of this nitrogen would appear as harmless molecular nitrogen (N_2). Instead, nitrogen in biomass is partitioned between N_2, ammonia (NH_3), and a small amount of hydrogen cyanide. These nitrogen compounds can be reacted with steam over a catalyst to reduce them to molecular nitrogen in a manner similar to the steam reforming of tar to light gases. In fact, tar and nitrogen compounds are sometimes decomposed in the same catalytic reactor. Relatively inexpensive Ni-based reforming catalysts can reduce ammonia in producer gas by over 75%. However, sulfur in the gas stream can quickly deactivate Ni-based catalysts unless they are protected by a guard bed of sulfur sorbent. Alternatively, since ammonia is soluble in slightly acidic solutions, it can be scrubbed from producer gas by a pH-adjusted water spray in a manner similar to the scrubbing of tar from producer gas.

Alkali metals commonly found in biomass include potassium and sodium. Potassium, an important nutrient in crop growth, is particularly prominent in biomass especially herbaceous feedstocks like grasses and corn stover. When biomass is heated, alkali metal compounds melt and some fraction of those evaporate at temperatures as low as 600°C. Alkali compounds transported out of the reactor,

usually in the form of chlorides, hydroxides, and sulfates, can condense on surfaces cooler than the gas stream, such as heat transfer surfaces, and form a sticky liquid film that adheres to fly ash. Over time, this leads to serious ash fouling. Furthermore, alkali can poison catalysts and corrode gas turbine blades even at very low concentrations.

Alkali can be removed from gas streams by cooling below its condensation temperature and then scrubbing out the resulting particulate matter in a manner similar to removal of tar aerosols. This can be done in conjunction with other unit operations of gas cleaning. Alternatively, removal of alkali from hot gas streams can be accomplished with solid sorbents known as getters. This approach is particularly attractive for gas turbines and certain fuel cell applications where cooling of the producer gas is to be avoided for thermodynamic reasons.

The occurrence of chlorine in biomass is species dependent. During combustion, most chloride is released as hydrochloric acid (HCl) although some reacts with alkali metals to form volatile salts. Both acid and salts readily absorb in water to form corrosive solutions that rapidly corrode metal surfaces in processing equipment. This high solubility is the key to its removal using water scrubbers, which may simultaneously remove other contaminants. A number of sodium-rich minerals have been employed as HCl sorbent in hot gas cleaning operations.

Even after gas cleaning, the producer gas may require additional processing to obtain gas composition consistent with power generation or chemical synthesis. For example, most fuel cells are dependent on hydrogen-rich gas streams for their operation. Pure hydrogen fuel has even been envisioned for gas turbine cycles in an effort to reduce greenhouse gas emissions into the atmosphere. Also, producer gas to be used for catalytic synthesis of hydrocarbons typically requires H_2:CO ratios to be increased to 2:1, after which it truly can be called "syngas."

Hydrogen enrichment can be achieved by combining steam with producer gas and passing the gas mixture over a catalytic bed. This promotes the reduction of water to hydrogen and the oxidation of carbon monoxide to carbon dioxide, a process known as the water–gas shift reaction (see Equation 8.7).

The water–gas shift reaction is exothermic, which means it is favored at low temperatures. To achieve commercially significant reaction rates, the process is conducted in two stages: a high-temperature reactor to rapidly move the reaction forward and a low-temperature reaction to achieve a higher overall yield of hydrogen. The water–gas shift reaction is widely employed by ammonia manufacturers, petroleum refiners, and other industries to produce hydrogen from natural gas and other fossil fuels.

8.3.4 Chemical Synthesis from Syngas

Clean, conditioned syngas, consisting of approximately two moles of hydrogen for every mole of carbon monoxide, provides the carbon, hydrogen, and energy

necessary to synthesize hydrocarbons as well as the oxygen necessary to synthesize oxygenated organic compounds like methanol and ethanol. Organic synthesis from this simple gaseous mixture was originally developed for the conversion of coal into methanol or synthetic gasoline. The process can also employ biorenewable resources as feedstock although the current low cost of fossil fuels has hampered the manufacture of biobased products by this method.

Two distinct approaches to convert syngas to chemicals are possible. The traditional approach involves the moderate temperature, high-pressure catalytic synthesis of methanol or synthetic gasoline. A more recently developed approach employs microorganisms that are able to grow on one-carbon compounds to convert syngas into organic acids or alcohols.

Catalytic Synthesis

Catalysts have been developed for the synthesis of a wide variety of chemicals from syngas. Those considered in this section include methanol, ammonia, dimethyl ether (DME), mixed alcohols, and Fischer–Tropsch (F–T) liquids.

Methanol (CH_3OH) is commercially produced by reacting syngas over a copper–zinc catalyst at 5–10 MPa and 250°C.

$$CO + 2H_2 \rightarrow CH_3OH \tag{8.9}$$

From the standpoint of cost, methanol is among the most attractive fuel production options for syngas. It is unlikely to find wide acceptance as fuel, though, because of its toxicity. It remains one of the largest commodity chemicals produced in the world. It is the building block for a wide variety of chemicals including synthetic gasoline via DME, as subsequently described.

Ammonia (NH_3) has been proposed as a propane-like fuel that can be produced from hydrogen and distributed as a compressed liquid using production and distribution technology developed for the nitrogen fertilizer industry. The exothermic reaction of hydrogen and nitrogen to produce ammonia favors high pressures and low temperatures:

$$N2 + 3H_2 \rightarrow 2NH_3 \tag{8.10}$$

Complete reaction would require pressures of 80 MPa and reaction temperatures below 200°C. Practical considerations require operation at higher temperatures and lower pressures. The Haber–Bosch process employs an iron-based catalyst at 20 MPa and 500°C to achieve a relatively modest 10–20% molar yield of ammonia, but the process is made economically feasible through recycling of unreacted gases and energy recovery. Sulfur readily poisons the iron-based catalyst used to facilitate this reaction. Because the hydrogen is generally obtained through steam reforming and water–gas shift reactions that also employ sulfur-sensitive catalysts, sulfur removal is usually accomplished ahead of hydrogen production.

The energy lost in transforming three molecules of hydrogen into two molecules ammonia would appear to be relatively modest: 87% of the chemical energy of the hydrogen appears in the chemical energy of the ammonia. However, the nitrogen for this fuel comes from liquefying air, an energy intensive process. Several energy intensive processes in ammonia manufacture bring the energy tab to 650 kJ/mol of ammonia produced. This may be justified when the product is fertilizer, but it does not compare favorably to the 316 kJ/mol of energy released when the ammonia is burned as fuel.

Methane can be catalytically generated from syngas by reacting it over nickel catalyst at low temperature and high pressure to promote the exothermic reactions:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{8.11}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{8.12}$$

Synthetic natural gas from coal by this process has been demonstrated on the commercial scale although the price of production is too high to be more widely deployed at this time.

Post-gasification synthesis to methane could be eliminated if methane was generated as the main product of gasification. This can be achieved by gasifying biomass in the presence of externally generated hydrogen, which reacts with carbon and carbon monoxide to form methane:

$$C + 2H_2 \rightarrow CH_4 \tag{8.13}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{8.14}$$

Known as hydrogasification, this exothermic process requires catalysts and operation at low temperatures and high pressures. The process has not achieved commercial status because suitable low-cost catalysts have yet to be developed.

Dimethyl ether has the chemical formula CH_3OCH_3. It can be produced either directly from syngas or indirectly through the dehydration of syngas-derived methanol by reactions at high pressure over catalysts. DME can be dehydrated over a zeolite catalyst to yield gasoline by the energy efficient "methanol-to-gasoline" (MTG) process developed by Mobil. MTG has been commercially demonstrated in New Zealand using syngas generated from the steam reforming of natural gas. Although yielding high-octane gasoline, the products include a high-melting-point hydrocarbon that can clog fuel injectors.

Synthesis of ethanol (C_2H_5OH) and higher alcohols is also possible from syngas. Efforts in Germany during World War II to develop alternative motor fuels discovered that iron-based catalysts could yield appreciable quantities of water-soluble alcohols from syngas. Some researchers have advocated the use of "mixed alcohols" as transportation fuels because the product typically contains a mixture of methanol, ethanol, 1-propanol, and 2-propanol. The process was commercialized

in Germany between 1935 and 1945 but eventually abandoned because of the increased availability of inexpensive petroleum. Working at pressures of around 5 MPa and temperatures in the range of 220–370°C, researchers have developed catalysts with selectivity to alcohols of over 95%, but production of pure ethanol has been elusive.

Mixed alcohol synthesis has not been commercialized due to poor product selectivity and low syngas conversion. On a single pass, about 10% of syngas gets converted with most of the product composed of methanol. Recycling methanol aids the production of higher alcohols. Generating revenue from higher alcohols would be important for the successful commercialization of this process.

Fischer–Tropsch liquids are synthetic alkane hydrocarbons produced from syngas by the action of metal catalysts at elevated pressures. Depending on the types and quantities of F–T products desired, either low- (200–240°C) or high-temperature (300–350°C) synthesis is used with either an iron (Fe) or cobalt catalyst (Co). Additional processing of the F–T products yields diesel or gasoline. F–T technology was extensively developed and commercialized in Germany during World War II when it was denied access to petroleum-rich regions of the world. Likewise, when South Africa faced a world oil embargo during its era of apartheid, it employed F–T technology to sustain its national economy from indigenous sources of coal. F–T catalysts are readily poisoned by sulfur, nitrogen, and chlorine at concentrations below one part per million. Thus, removal of contaminants ahead of the synthesis reactors is an important and expensive part of F–T synfuels' plant.

Biocatalytic Synthesis

Certain microorganisms, known as unicarbontrophs, are able to grow on one-carbon compounds as the sole source of carbon and energy. These include some of the same microorganisms involved in anaerobic digestion of polysaccharides. Acetogens can convert CO or mixtures of CO and H_2 to fatty acids and, in some cases, alcohols. Both types of microorganisms are thought to involve a common reaction pathway that disproportionates CO and produces acetyl CoA as an intermediate. Methanogens can produce methane from mixtures of CO, CO_2, and H_2. Thus, syngas can be biologically converted to a variety of fuels and chemicals including ethanol, methane, acetic acid, butyric acid, and butanol.

Clostridium ljungdahlii, a gram-positive, motile, rod-shaped anaerobic bacterium isolated from chicken waste, has received particular attention for its ability to co-metabolize CO and H_2 to form acetic acid (CH_3COOH) and ethanol (CH_3CH_2OH):

$$4CO + 2H_2O \rightarrow CH_3COOH + 2CO_2 \quad (8.15)$$

$$4H_2 + 2CO_2 \rightarrow CH_3COOH + 2H_2O \quad (8.16)$$

$$6CO + 3H_2O \rightarrow CH_3CH_2OH + 4CO_2 \quad (8.17)$$

$$6H_2 + 2CO_2 \rightarrow CH_3CH_2OH + 3H_2O \quad (8.18)$$

The wild-type strain of *C. ljungdahlii* produced an ethanol-to-acetate ratio of only 0.05 with maximum ethanol concentration of 0.1 g/L. This ratio is very sensitive to acidity; decreasing pH to 4.0 increased the ratio to 3.0. Other adjustments to the culture media and operating conditions nearly eliminated acetate production and increased ethanol concentration to 48 g/L after 25 days.

This gasification/fermentation route to biobased products from lignocellulosic feedstocks has several advantages compared to hydrolytic/fermentation techniques described in Chapter 7. Gasification allows very high conversion of lignocellulosic biomass to usable carbon compounds (over 90%), whereas hydrolysis utilizes only the carbon associated with the carbohydrate (approximately 60% of the total). Gasification yields a uniform product regardless of the biomass feedstock employed, whereas hydrolysis yields a product dependent on the content of cellulose, hemicellulose, and lignin in the feedstock. Finally, since the syngas is produced at high temperatures, gasification yields an inherently aseptic carbon supply for fermentation.

Biological processing of syngas has several advantages compared to chemical processing. The H_2:CO ratio is not critical to biological processing of syngas, thus making unnecessary the water–gas shift reaction to increase the hydrogen content of biomass-derived syngas. Whereas catalytic syngas reactors require high temperatures and pressures, biocatalysts operate near ambient temperature and pressure. Also, biocatalysts are typically more specific than inorganic catalysts.

Syngas fermentation faces several challenges before commercial adoption. Syngas bioreactors exhibit low volumetric productivities due, in part, to low cell densities. Cell recycle and immobilization of cells in bioreactors are possible solutions to this problem. Mass transfer of syngas into the liquid phase is also relatively slow. In commercial-scale aerobic fermentations, mass transfer of oxygen is generally the rate-limiting process. The problem will be exacerbated for syngas fermentations since the molar solubilities of CO and H_2 are only 77% and 65% of that of oxygen, respectively. Possible solutions to this mass transfer limitation are dispersion of syngas into microbubbles of 50 μm diameter and growth of biofilms on gas permeable membranes.

8.4 Fast Pyrolysis

Pyrolysis is the rapid thermal decomposition of organic compounds in the absence of oxygen to produce liquid, gas, and char. The rate of heating, the maximum temperature achieved, the duration of heating, and the manner in which products are cooled strongly influence product distribution. Heating rate is determined by a combination of biomass particle size and physical factors within the reaction environment. Pyrolysis of relatively large pieces of biomass at temperatures around 500°C in a quiescent pile is characterized as slow pyrolysis and produces high yields of char. Pyrolysis of small- to medium-sized pieces of biomass at temperatures above

800°C in a reactor that promotes good gas exchange yields mostly light gases, as described in the section on gasification. Pyrolysis of very small particles (<1–3 mm) at temperatures between 300°C and 500°C in reactors that achieve fast heating of biomass and rapid cooling of products is known as fast pyrolysis and produces primarily liquid product. Fast pyrolysis is attractive because the liquid has prospects as heating fuel, a source of chemicals, and feedstock for refining into liquid transportation fuels.

Fast pyrolysis can be thought of as direct liquefaction of biomass although the combination of elevated temperature and relatively modest pressure (often atmospheric) causes any compounds that normally would be liquid at ambient conditions (25°C, 0.1 MPa) to vaporize. The gas stream exiting a fast pyrolyzer contains entrained solid particles of char, noncondensable gases, condensable organic vapors, liquid aerosols, and water vapor. The char consists of carbonaceous residue from the pyrolyzed biomass, mostly elemental carbon, and mineral matter intrinsic (nutrients) or extrinsic (dirt) to the biomass. The noncondensable gases are mostly CO and CO_2 with smaller amounts of H_2 and light alkanes and alkenes. For pyrolysis of lignocellulosic biomass, the condensable organic vapors contain a wide variety of light oxygenated organic compounds, mostly derived from the carbohydrate content of the biomass. Some portion of the condensable organic vapors are phenolic monomers and possibly dimers derived from the lignin in lignocellulosic biomass. The aerosols consist of high-molecular-weight compounds with vapor pressures so low they can only exist in the pyrolysis gas stream as liquid. These include phenolic oligomers derived from lignin and, somewhat surprisingly, sugars or anhydrosugars derived from cellulose and hemicellulose.

Pyrolysis liquid, commonly known as bio-oil, is the combination of condensable vapors, aerosols, and water vapor recovered from the pyrolysis gas stream, yielding between 50 and 75 wt% liquid from lignocellulosic biomass. The recovered bio-oil, as shown in Figure 8.6, is a dark, viscous liquid containing 15–20 wt% water. Bio-oil is best described as an emulsion of lignin-derived phenolic oligomers (sometimes referred to as "water insolubles" or "pyrolytic lignin") in an aqueous phase composed primarily of carbohydrate-derived compounds. The bio-oil also contains a small amount of suspended char particles carried over in the gas flow to the bio-oil recovery system.

The chemical compositions of bio-oil from softwood (white spruce) and hardwood (poplar) are compared in Table 8.3. The organic phase is listed as "pyrolytic lignin" and is not analyzed for individual components because of its oligomeric nature, but it includes phenolic monomers, dimers, trimers, and tetramers with various functionalities, especially methyl, methoxy, and vinyl. As the result of these reactive phenolic compounds, the organic phase slowly polymerizes during storage, increasing the viscosity and the instability of the emulsion, which may lead to phase separation of the bio-oil. The phenolic oligomers are also responsible for thermal instability of bio-oil when heated during upgrading.

FIG. 8.6 Bio-oil from the fast pyrolysis of lignocellulosic biomass.

The aqueous phase consists mostly of carbohydrate-derived compounds including alcohols, aldehydes, carboxylic acids, esters, furans, pyrans, ketones, monosaccharides, and anhydrosugars, which are responsible for the high oxygen content of the bio-oil. It also contains a small amount of phenolic monomers, which are slightly soluble in water. The bio-oil is highly acidic due to the carboxylic acids, mostly derived from the acetyl group side chains of hemicellulose.

Assuming conversion of 70% of the biomass feedstock to liquid on a weight basis, yields of pyrolysis oil are about 560 L/ton of biomass. The higher heating value of bio-oil ranges between 17 and 20 MJ/kg with liquid densities of about 1280 kg/m^3.

Pyrolysis liquid can be used directly as a substitute for industrial heating oil although it is too corrosive and unstable for commercial or residential applications. In some circumstances, it is also suitable as fuel for combustion turbines or modified diesel engines in stationary power applications. Use as fuel oil substitute is complicated by long ignition delays and varying impacts of water, char, and volatiles content on relative burn rates. The viscosity, density, and surface tension of bio-oil are significantly greater than those of diesel fuel, suggesting that poor atomization might hamper efficient ignition and combustion.

Table 8.3 Analysis of products from fast pyrolysis

	White Spruce	Poplar	Type of Compound
Moisture content, wt%	7.0	3.3	
Particle size, μm (max)	1000	590	
Temperature	500	497	
Apparent residence time	0.65	0.48	
Product yields, wt%, m.f.			
Water	11.6	12.2	
Char	12.2	7.7	
Gas	7.8	10.8	
Pyrolytic liquid	66.5	65.7	
Gas composition, wt%, m.f.			
H_2	0.02	–	
CO	3.82	5.34	
CO_2	3.37	4.78	
CH_4	0.38	0.41	
C_2 hydrocarbons	0.20	0.19	
C_3^+ hydrocarbons	0.04	0.09	
Pyrolytic liquid composition, wt%, m.f.			
Water-soluble compounds			
Oligosaccharides	–	0.70	Saccharides
Glucose	0.99	0.41	
Other monosaccharides	2.27	1.32	
Levoglucosan	3.96	3.04	Anhydrosugars
1,6-Anhydroglucofuranose	–	2.43	
Cellobiosan	2.49	1.30	
Glyoxal	2.47	2.18	Aldehydes
Methylglyoxal	–	0.65	
Formaldehyde	–	1.16	
Acetaldehyde	–	0.02	
Hydroxyacetaldehyde	7.67	10.03	
Furfural	0.30	–	Furans
Methylfurfural	0.05	–	
Acetol	1.24	1.40	Ketones
Methanol	1.11	0.12	Alcohols
Ethylene glycol	0.89	1.05	
Acetic acid	3.86	5.43	Carboxylic acids
Formic acid	7.15	3.09	
Water soluble—total above	34.5	34.3	
Pyrolytic lignin	20.6	16.2	
Unaccounted	11.4	15.2	
Organic liquid	66.5	65.7	

Source: Piskorz, J., Scott, D.S., and Radlein, D. (1988) *Pyrolysis Oils from Biomass* (eds. E.J. Soltes and T.A. Milne), pp. 167–178. ACS Symposium Series 376. Washington, DC: American Chemical Society.

Bio-oil cannot be used directly as transportation fuel. Like petroleum, it must be refined to molecules compatible with high-performance spark ignition, compression ignition, and gas turbine engines. The diverse composition, low molecular weight, high oxygen content, and high acidity of the aqueous phase and the high viscosity, low volatility, and high reactivity of the organic phase complicate the

removal of oxygen (deoxygenation) and refining to fuel-range molecules. The upgrading of bio-oil to transportation fuels is described later in this chapter.

Recovery of high-value chemicals is another possibility, suggesting an integrated approach to production of both chemicals and fuel. For example, levoglucosan is obtained at high yields upon fast pyrolysis of pure cellulose or starch. Even woody or herbaceous biomass can yield significant levoglucosan if metal ions, particularly potassium, are removed or deactivated prior to pyrolysis. Levoglucosan is considered a potential building block for synthesis of dextrin-like polymers, pharmaceuticals, pesticides, and surfactants. Microorganisms have been identified or genetically modified to ferment levoglucosan to citric acid and ethanol, which may be an attractive source of these chemicals if the levoglucosan is obtained from inexpensive lignocellulosic materials. Considering that lignin is both the "glue" that holds together cellulose strands in plant fibers and an antimicrobial agent that protects plant fibers from pests, it is not surprising that phenol has commercial and historical applications in the production of adhesives and antiseptics.

8.4.1 Fundamentals of Pyrolysis

Cellulose, hemicellulose, and lignin have distinctive thermal decomposition behaviors that depend upon heating rate. Under conditions of relatively low heating rate and high ventilation rates with inert sweep gas, hemicellulose is the first constituent to decompose, beginning at 220°C and substantially completing by 315°C. Cellulose does not start to decompose until about 315°C. If volatiles are quickly removed from the reaction zone, cellulose is mostly converted to condensable organic vapors and aerosols once 400°C is attained. High pressures and the absence of ventilation promote char and gas-forming reactions at the expense of condensable organic vapors. Lignin begins to decompose at 160°C but extends to 900°C, yielding a solid residue approaching 40 wt% of the original sample.

Although biomass pyrolysis has traditionally been viewed as random decomposition reactions, recent research is proving that deliberate depolymerization of plant compounds to desired products is possible. For example, scission of the pyranose rings making up the polymeric chains of cellulose and hemicellulose yields mostly light oxygenated compounds like carboxylic acids, aldehydes, ketones, and furans. Experiments on the pyrolysis of pure cellulose, however, reveal that the glycosidic bonds between the rings are preferentially broken, producing predominately 1,6-anhydro-β-D-glucopyranose ($C_6H_{10}O_5$), a singly dehydrated glucose molecule known as levoglucosan. In fact, cellulose is visually observed to melt when exposed to high temperatures. Like sugar, this melted levoglucosan might be expected to polymerize and dehydrate by secondary reactions to form char and light gases. The fact that levoglucosan is found in bio-oil suggests that it is able to escape from the reaction zone before this happens. Some researchers hypothesize that levoglucosan or oligosaccharides are thermally ejected as aerosols out of

the pyrolyzer. However, a simpler explanation is that levoglucosan simply evaporates from the pyrolyzer. Whereas most sugars have virtually no vapor pressure, anhydrosugars have measurable vapor pressures at pyrolysis temperatures, allowing them to evaporate before they carbonize. Levoglucosan vapors are relatively stable, allowing them to be transported out of the pyrolysis reactor and recovered. Because levoglucosan can be readily hydrolyzed to glucose, this suggests a pathway for the thermal depolymerization of cellulose to sugars.

The fact that cellulose in the form of lignocellulosic biomass produces only modest amounts of levoglucosan compared to pure cellulose indicates other processes are also occurring. This appears to arise from the naturally occurring alkali and alkaline earth metals (AAEM) found in most biomass, which catalyze ring scission of the pyranose rings in cellulose to yield mostly light oxygenates. The competing processes of glycosidic bond breaking and pyranose ring scission are illustrated in Figure 8.7. Thoroughly washing biomass to remove AAEM prior to pyrolysis dramatically enhances the yield of levoglucosan, but such washing is not a practical operation in large-scale processing. More promising is infusion of small amounts of mineral acid into the biomass, converting the AAEM into thermally stable salts that are no longer effective at catalyzing ring scission, dramatically increasing anhydrosugar production.

Hemicellulose also shows significant thermal depolymerization in the absence of AAEM (see Figure 8.8). Recall that hemicellulose is a large number of het-

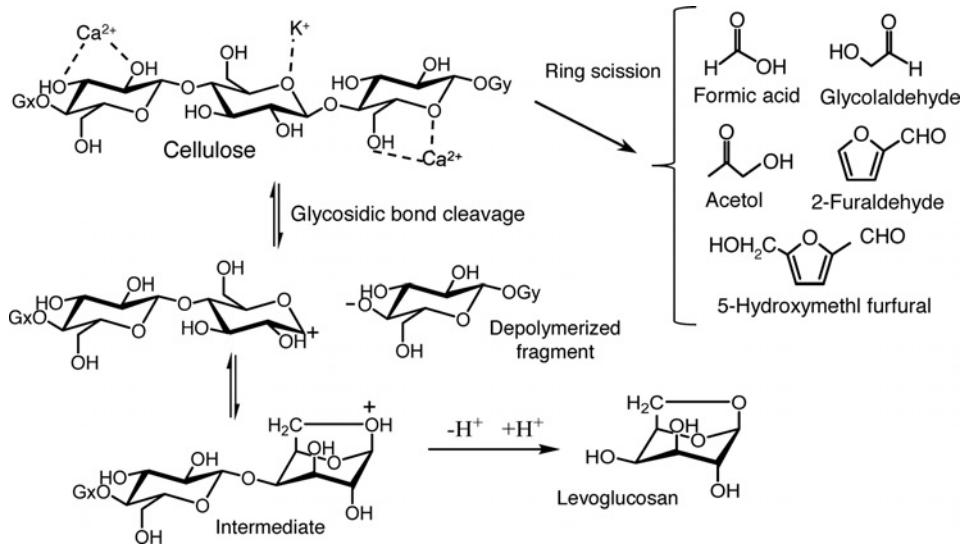

FIG. 8.7 Competing mechanisms of cellulose depolymerization to levoglucosan and alkali/alkaline earth metal catalyzed ring scission to light oxygenated compounds. Adapted from Patwardhan, P.R., Satrio, J.A., Brown, R.C., and Shanks, B.H. (2010) Influence of inorganic salts on the primary pyrolysis products of cellulose. *Bioresource Technology*, 101, 4646–4655.

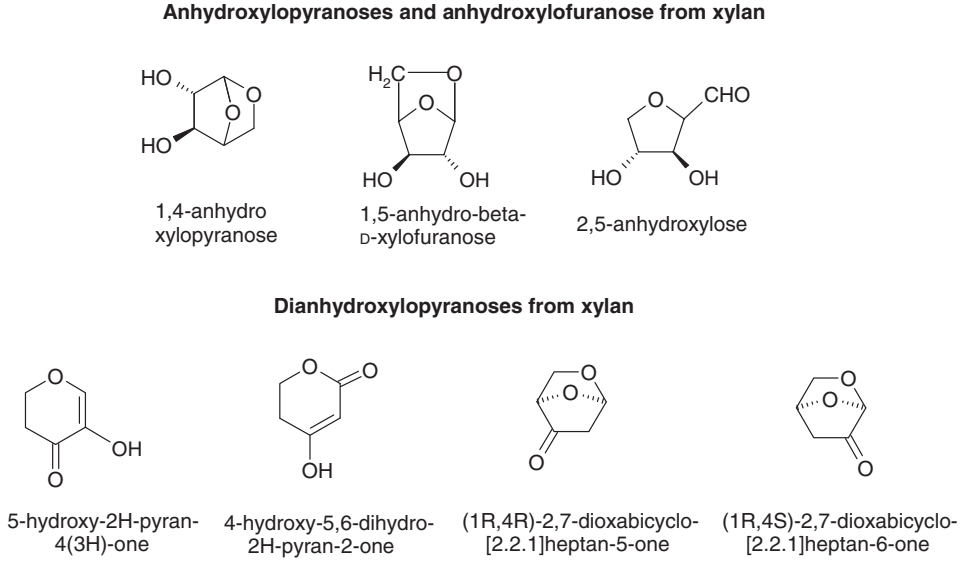

FIG. 8.8 Depolymerization and dehydration products from the pyrolysis of pure hemicellulose. Adapted from Patwardhan, P.R., Brown, R.C., and Shanks, B.H. (2011) Product distribution from the fast pyrolysis of hemicellulose. *ChemSusChem*, 5, 636–643.

eropolysaccharides. This discussion will focus on xylan, the predominant hemicellulose in lignocellulosic biomass, which consists of a backbone of β-(1→4)-D-xylopyranose ($C_5H_{10}O_5$) with a variety of side chains. As might be expected, some of the depolymerization products are singly dehydrated xyloses known as anhydroxyloses, including the isomers 1,4-anhydro-xylopyranose; 1,5-anhydro-β-D-xylofuranose; and 2,5-anhydroxylose ($C_5H_8O_4$). Even more prominent are pyrans and tetrahydropyrans, which are dianhydroxylopyranoses (doubly dehydrated xylose), including 5-hydroxy-2*H*-pyran-4(3*H*)-one; 4-hydroxy-5,6-dihydro-2*H*-pyran-2-one; (1*R*,4*R*)-2,7-dioxabicyclo-[2.2.1]heptan-5-one; and (1*R*,4*S*)-2,7-dioxabicyclo-[2.2.1]heptan-6-one. The depolymerization products include significant amounts of acetic acid derived from the acetyl and possibly the 4-*O*-methylglucuronic acid side chains of the xylan.

In the presence of AAEM, these depolymerization/dehydration products are not as prevalent. Instead, products typical of ring scission are evident, including light oxygenates and noncondensable gases like CO_2. Products of severe dehydration reactions are evident including 2-furaldehyde ($C_5H_4O_2$), which is triply dehydrated xylose, and char.

If the polysaccharide in lignocellulose can be converted into anhydrosugars at high yields, this would enhance upgrading of bio-oil to fuels. Anhydrosugars can be hydrolyzed to monosaccharides and fermented to ethanol or butanol. Alternatively,

it is more attractive to catalytically upgrade anhydrosugars or sugars (C5–C6) to fuel-range molecules (C5–C22) than to start with light oxygenates (C2–C3).

Lignin, like the polysaccharide in lignocellulosic biomass, also depolymerizes upon rapid heating. Some researchers hypothesize that lignin partially depolymerizes to large fragments that are thermally ejected from the pyrolysis zone, allowing them to be recovered in bio-oil. More consistent with the experimental evidence is depolymerization of lignin to highly substituted phenolic monomers and dimers that are sufficiently volatile to evaporate. The side chains of these phenolic monomers include methyl, methoxy, carboxylic, ethyl, and vinyl groups. Figure 8.9 illustrates some of the substituted phenolic monomers observed as products of pyrolysis. These functionalities impart a wide variety of physical and chemical properties to the phenolic compounds including acidity, boiling point, solubility, and reactivity.

Interestingly, analysis of bio-oil reveals relatively few phenolic monomers and dimers compared to phenolic oligomers in the bio-oil. This is the result of the high reactivity of side chains on the phenolic compounds, which rapidly repolymerize by secondary reactions in the gas phase. The resulting oligomers are no longer volatile, causing them to condense as liquid aerosols, physically evident in the pyrolysis gas stream as light-scattering white smoke. Supporting this theory of

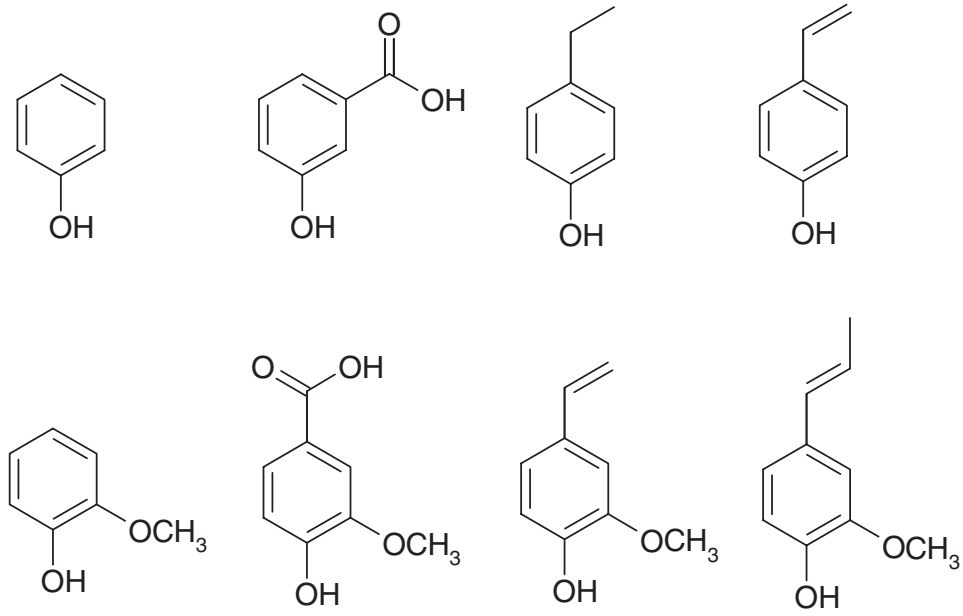

Fig. 8.9 Phenolic monomers from the depolymerization of lignin illustrating methyl (–CH3), methoxy (–OCH3), carboxylic (–COOH), ethyl (–CH2–CH2-) and vinyl (–CH–CH2) functionalities. Adapted from Patwardhan, P.R., Brown, R.C., and Shanks, B.H. (2011) Understanding the fast pyrolysis of lignin. *ChemSusChem*, 4, 1629–1636.

repolymerization in the gas phase is the observation that phenolic oligomers in bio-oil, known as pyrolytic lignin, continue to polymerize at room temperature over the course of hours or even months.

Lignin is the primary source of char during pyrolysis. This is the result of the relatively slow rate of lignin depolymerization to volatile monomers, allowing reactive lignin fragments to repolymerize and subsequently dehydrate to char. As with cellulose, char formation from lignin can be suppressed, although not eliminated, by rapidly heating the biomass and removing the product vapors from the pyrolysis zone.

In principle, lignin-derived molecules are attractive because of their relatively low oxygen content compared to carbohydrates. Phenolic monomers and dimers also have attractive carbon numbers (C6–C20) for production of fuel-range molecules (C5–C22). In practice, many of the lignin-derived compounds in bio-oil are phenolic trimers and tetramers or even larger oligomers. These have viscosities too high and volatilities too low to be easily hydrotreated. Furthermore, their tendency to polymerize and dehydrate when heated also leads to low carbon yields. If the secondary reactions responsible for repolymerization of phenolic monomers could be controlled to produce molecules no larger than dimers, the lignin-derived fraction of bio-oil would be more attractive as refinery feedstock. The secondary reactions of lignin pyrolysis need to be better understood before this possibility is achieved.

8.4.2 Pyrolysis Systems

Pyrolysis systems convert raw biomass feedstock into pyrolysis streams containing noncondensable gases, condensable vapors, aerosols, and char and recover these coproducts as separate streams of solids, one or more liquids, and gases. A wide variety of pyrolysis systems have been developed, which can be categorized as (conventional) fast pyrolysis, catalytic pyrolysis, and hydropyrolysis, as described below. Further classifications are possible based on the method of transferring heat into the reactor and removing products, a description of which is beyond the scope of this introduction to the field.

Fast Pyrolysis

Production of pyrolysis oils and coproducts is illustrated in Figure 8.10. Lignocellulosic feedstock, such as wood or agricultural residues, is milled to fine particles of less than 1 mm diameter to promote rapid reaction, on the order of 1 second. The particles are entrained in an inert gas stream and transported to the pyrolysis reactor. A fluidized bed reactor is illustrated in Figure 8.10 although other kinds of reactors, like auger and entrained flow reactors, can be used as long as they provide the high heat transfer rates and rapid vapor disengagement required for high bio-oil yields. An external source of heat must be supplied to the pyrolysis reactor. Heat exchange can be achieved by either indirect contact (heat transfer

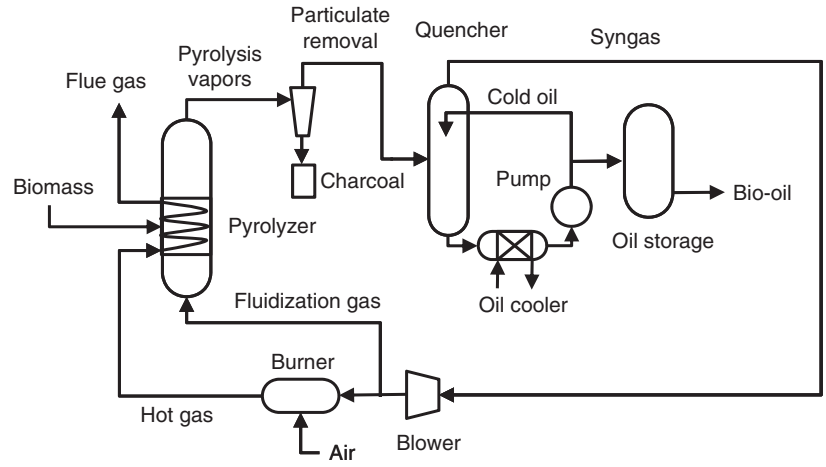

FIG. 8.10 Fast pyrolysis system.

across heat exchange surfaces) or direct contact (circulation of hot sand or steel shot into the pyrolysis reactor). Within the reactor, the particles are rapidly heated and converted into condensable vapors, noncondensable gases, and solid char particles. In fluidized beds and entrained flow reactors, the products are together transported out of the reactor (in auger reactors a large portion of the char is separately removed from the reactor). Those products transported out of the reactor with the pyrolysis gas stream enter a cyclone operating above the condensation temperature of pyrolysis vapors, which allows entrained char particles to be separated.

Vapors and gases are transported to a bio-oil recovery system where they are rapidly cooled to prevent further reaction. Illustrated in Figure 8.10 is a direct-contact quench vessel where a spray of cold pyrolysis liquid cools and condenses the vapors. Other possibilities for bio-oil recovery include arrangements of condensers and electrostatic precipitators to efficiently recover both vapors and aerosols from the pyrolysis stream. The noncondensable gases, which include flammable CO, H_2, and CH_4, are burned in air to provide heat for the pyrolysis reactor. The char is also partly or fully consumed in raising heat for the pyrolyzer.

Bio-oils from such conventional fast pyrolysis systems require extensive deoxygenation to make them suitable as transportation fuel. Alternative pyrolysis processes are described below that partially deoxygenate and otherwise improve the quality of the bio-oil for upgrading to fuels.

Catalytic Pyrolysis

Catalytic pyrolysis uses catalysts either within the pyrolysis reactor (*in situ* catalytic pyrolysis) or immediately downstream of the pyrolysis reactor (*ex situ* catalytic

pyrolysis) to promote the formation of desirable fuel precursor molecules. It is distinguished from catalytic upgrading of bio-oil, which occurs after the bio-oil has been recovered as a liquid. Considering the high temperatures and atmospheric pressure commonly employed, catalytic pyrolysis is a vapor phase process, with the catalysts acting on the volatiles released from the pyrolyzing biomass.

Catalysts are able to accelerate desired chemical reactions, breaking and rearranging molecular bonds and adding or subtracting atoms from reactants. Catalyzing reactions before pyrolysis products have condensed to bio-oil has the advantage of processing the primary products of pyrolysis ahead of uncontrolled secondary reactions such as ring scission or repolymerization. Recall also that bio-oil is viscous and nonvolatile, complicating its upgrading, which vapor-phase processing may avoid.

One of the goals of catalytic pyrolysis is to partially or fully deoxygenate carbohydrate-derived compounds through decarbonylation (removal of CO) and decarboxylation (removal of CO_2), at least to the extent of making the product molecules water insoluble (less polar) and less acidic. The less oxygen, water, and acidity the products contain, the more compatible they are with petroleum refining processes. Another goal is to stabilize the phenolic monomers and dimers released from depolymerizing lignin to prevent them from forming large oligomers responsible for the low volatility and high viscosity of conventional bio-oil.

In situ catalytic pyrolysis is attractive because the catalyst is intimately contacted with the pyrolyzing biomass, assuring that primary rather than secondary products of pyrolysis are involved in catalytic reaction. It has the disadvantage that optimal pyrolysis and catalysis conditions may not be achieved in a single reactor. Close contact of minerals or metal salts with the catalyst in the pyrolysis bed may also poison the catalysts and it may be difficult to recover spent catalysts for recycling. *Ex situ* overcomes these disadvantages by separating pyrolysis and catalysis. However, the transport time between the two reactors may allow undesired secondary reactions to occur. Of particular concern is the formation of phenolic oligomers, which are likely to foul *ex situ* catalysts.

Pyrolytic catalysis can be characterized as mild or severe. The goal of mild catalytic pyrolysis is to sufficiently reduce the acidity and polarity of the bio-oil through deoxygenation to allow it to be processed in a petroleum refinery. Severe deoxygenation attempts to produce hydrocarbon molecules. An example of severe catalytic pyrolysis uses acidic zeolite catalysts to crack and dehydrate carbohydrate to aromatic hydrocarbons, including benzene, toluene, and xylene (BTX), which are high-value petrochemicals and octane boosters for gasoline. Although aromatic yields are as much as 17 wt%, coke yields are unattractively high at present. Catalytic pyrolysis does not use hydrogen or other gaseous reducing agents in part because of the difficulty of operating reactors that process solid fuels at the high pressures thought important for these reducing agents to be effective.

Hydropyrolysis

Hydropyrolysis pyrolyzes biomass in the presence of both catalyst and high-pressure hydrogen to produce highly deoxygenated molecules, often hydrocarbons. Although not well understood, the addition of high-pressure hydrogen to a pyrolysis reactor in the presence of a catalyst probably accomplishes both hydrodeoxygenation of pyrolysis vapors and stabilization of lignin-derived phenolic compounds, preventing them from forming high-molecular-weight oligomers that would require even more severe reactions conditions to crack into fuel-range molecules. The advantage of hydropyrolysis over catalytic pyrolysis is carbon yield. Although, like catalytic pyrolysis, some coke is formed, oxygen is removed as water rather than as carbon monoxide and carbon dioxide, preserving more carbon in the fuel products. The disadvantage is operation at high pressure, up to 5 MPa, which makes difficult the continuous feeding of biomass into the pyrolyzer. Although the products are very attractive from the standpoint of refining into fuels, further development of pressurized feeding systems for solid biomass is required to make this process feasible.

8.5 Solvolysis

Solvolysis in the most general sense is the interaction of a solvent with a solid or liquid reactant to produce chemical products. Although the reference to solvent suggests that the reactant and/or products are dissolved in the solvent, this is not necessarily the case. Sometimes both solvent and reactant participate in the chemical reaction, but in other cases the solvent merely serves as heat or mass transfer medium. Solvolysis often involves the thermal decomposition of complex organic compounds, in which case it can be thought of as "pyrolysis in a solvent," although specific reactions and products can be quite different for pyrolysis and solvolysis.

Both polar and nonpolar solvents can be used. Among polar solvents, both protic and aprotic solvents have application (protic solvents can participate in hydrogen bonding or even donate hydrogen to the reaction). When water is used as solvent, especially convenient when processing high-moisture feedstocks, solvolysis is referred to as hydrothermal processing. Sometimes mixtures of solvents are used, frequently to produce a biphasic system of polar and nonpolar phases to improve product separation and recovery. Both homogeneous (liquid) and heterogeneous (solid) catalysts have been explored to enhance yields and improve product selectivity.

Like some other thermochemical conversion technologies, solvolysis was originally developed to convert (solid) coal into liquid fuels. This coal-to-liquid process is referred to as direct liquefaction, in contrast to indirect liquefaction achieved by

first gasifying coal and then catalytically synthesizing liquid fuels from the gas. The term "solvent liquefaction" has also been applied, but more generally, solvolysis can produce solids and gases as well as liquid products.

Solvolysis is attractive for the wide range of products that can be produced from a given feedstock by controlling the processing conditions, including the choice of solvent. Bio-oil from solvolysis usually has lower oxygen and water content than bio-oil from pyrolysis; therefore, it has some advantages in upgrading to transportation fuels. Solvolysis requires further development before it becomes commercially significant. First is the need to continuously process solid biomass at elevated pressures, which prevents solvent from evaporating during reaction. Pressures can be as high as 18 MPa for systems using water and operating at 350°C. The second disadvantage is the cost of nonaqueous solvents, which are expensive to use unless they are efficiently recovered and reused or generated by the process.

8.5.1 Direct Liquefaction of Lignocellulose

Direct liquefaction was first developed in Germany during the 1910s to convert coal into liquid hydrocarbons. Although the original patents claimed the process was applicable to a wide variety of solid carbonaceous feedstocks, there is no evidence that biomass was ever evaluated in a continuous process. Direct liquefaction of coal, on the other hand, was put into commercial practice in Germany during World War II when the country was denied access to petroleum resources.

Known as the Bergius process after its inventor, direct liquefaction was accomplished by slurring coal with a tarry solvent and reacting the mixture with hydrogen over a metal catalyst at 490°C and 23 MPa. The solvent promoted heat and mass transfer and shuttled hydrogen from the gas phase to the coal. The high temperature thermally ruptured carbon–carbon bonds, allowing hydrogen to react with the coal, increasing the H:C ratio required to produce liquid hydrocarbons. Operation at high pressure prevented evaporation of solvent and increased the partial pressure of hydrogen, which promoted reaction. The liquid, produced in yields of 40–60 wt%, was separated into a "middle distillate" that was further hydrogenated to produce gasoline-range molecules and "still bottoms" that were used as make-up solvent.

Efforts to directly liquefy biomass did not emerge until the 1970s, apparently inspired by the original Bergius process. Biomass mixed with hydrocarbon solvent is reacted with various catalysts at temperatures ranging from 230°C to 450°C and pressures from 7 to 50 MPa. When solvent serves as hydrogen donor, it is primarily to reduce the O:C ratio of the biomass-derived products rather than to increase its H:C ratio. Both hydrogen and carbon monoxide gases have been tested as reducing agents with the notion that biomass-derived producer gas might be

used to deoxygenate the biomass. Oxygen could also be removed through decarbonation or decarboxylation of the biomass without the addition of an external reducing agent.

In contrast to the single-phase liquid product produced from coal, direct liquefaction of lignocellulosic biomass yields two distinct phases of liquid product: a phenolic-rich, water-insoluble organic phase derived primarily from lignin and an aqueous phase derived mostly from carbohydrate and containing up to 30% of the original energy of the biomass. The organic phase, sometimes referred to as bio-oil, is partially deoxygenated and has lower moisture and higher heating value than pyrolysis-derived bio-oil. Differences between the two kinds of bio-oil are partly due to deoxygenation achieved by solvolysis, but they also reflect the presence of water in the pyrolysis-generated bio-oil. Direct liquefaction can produce a wide range of liquid products, including aliphatic and aromatic alcohols, phenols, hydrocarbons, substituted furans, and alicyclic compounds. Like coal-derived oil, the organic phase can be upgraded by reaction with high-pressure hydrogen in the presence of a catalyst, a process known as hydroprocessing.

8.5.2 Hydrothermal Processing of Lignocellulosic Biomass

Hydrothermal processing exploits enhanced solvent properties of compressed or supercritical water. Many organic nonpolar compounds become miscible with water under such condition, and the presence of H_3O^+ and OH^- ions in pressurized water serve as acid and base catalysts in the media. Hydrothermal processing of wet lignocellulose can produce extracted biomass components, fractionated biomass components, liquefied biomass, or gasified biomass depending upon the reaction conditions, often without catalysts (see Figure 8.11). As reaction temperature increases, higher pressures are required to prevent boiling of the water in the wet biomass.

At temperatures around 100°C, extraction of high-value plant chemicals such as resins, fats, phenolics, and phytosterols is possible. At 200°C and 2 MPa, fibrous biomass undergoes a fractionation process to yield cellulose, hemicellulose degradation products such as furfural or 5-hydroxy-methylfurfural (HMF), and lignin. Further hydrothermal processing can hydrolyze the cellulose to glucose. At 300–350°C and 12–18 MPa, biomass undergoes more extensive chemical reactions yielding a water-insoluble organic phase known as (hydrothermal processing) bio-oil. Although superficially resembling bio-oil from pyrolysis, it has lower oxygen content and is less miscible in water, making it more amenable to hydroprocessing. At 600–650°C and 30 MPa, the primary reaction product is gas, including a significant fraction of methane.

Continuous feeding of biomass slurries into high-pressure reactors and efficient energy integration represent engineering challenges that must be overcome before HTP results in a commercially viable technology.

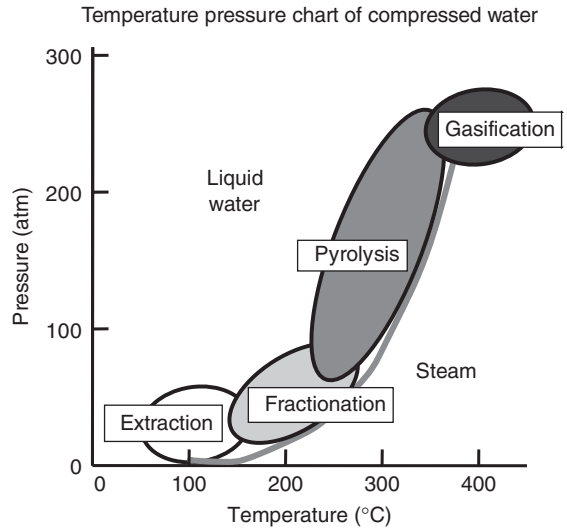

FIG. 8.11 Different operating regimes for hydrothermal processing: extraction, fractionation, pyrolysis, and gasification.

8.6 Chemical Upgrading to Transportation Fuels

Thermochemical or biochemical processing of herbaceous or woody biomass produces "deconstructed lignocellulosic biomass" that requires further processing to finished products. Deconstructed lignocellulosic biomass includes sugars or solubilized carbohydrate liberated from lignocellulosic biomass by acid or enzymatic hydrolysis or thermal depolymerization; and bio-oil from fast pyrolysis or solvolysis. They may exist as an emulsion of water-insoluble organic phase in an aqueous phase or separate phases of water-insoluble organics and aqueous solutions of soluble organic compounds. Usually the liquids contain significant oxygen although partial deoxygenation may have occurred in producing the deconstructed lignocellulosic biomass. The goal of chemical upgrading is to convert these feedstocks into either commodity chemicals and finished fuels or blendstocks suitable for additional upgrading in a conventional petroleum refinery. In that respect, deconstructed lignocellulose may be thought of as “bio-crude.”

Early in the development of pyrolysis and solvolysis, it was hoped that upgrading technologies developed over 100 years of petroleum refining could be used to upgrade bio-oils into finished fuels. However, there are important differences between unrefined petroleum, also known as crude oil, and deconstructed lignocellulosic biomass that prevents a simple translation of upgrading technologies. Unrefined petroleum is a mixture of mostly alkane and aromatic hydrocarbons containing few functional groups. As a result of this chemical composition, unrefined

petroleum is nonpolar, contains only a small amount of unstable compounds, and is relatively volatile. The petroleum industry exploits these properties in refining petroleum to fuels. Crude oil often contains water, salts, and insoluble minerals, which need to be removed before processing. Because petroleum is nonpolar and water is polar, they are immiscible in one another allowing water to be used to wash salts and other minerals out of the petroleum, followed by simple phase separation to remove the water. Because petroleum is relatively stable and volatile, it can be heated and separated into hydrocarbon fractions according to boiling point, which can be upgraded by the well-established refining processes.

Deconstructed lignocellulosic biomass, on the other hand, is a mixture of sugars and light oxygenates derived from carbohydrate- and lignin-derived aromatic compounds. The carbohydrate-derived compounds are polar and include diverse oxygen-rich functionalities. With the exception of anhydrosugars, saccharides have virtually no volatility. The lignin-derived compounds are aromatic but contain significant functionalities and often exist as nonvolatile, highly reactive oligomers. Deconstructed biomass often contains significant water, which readily dissolves the polar, carbohydrate-derived compounds, making it impossible to remove water and dissolved minerals before upgrading. The lack of volatility and high reactivity of many of the constituents makes impossible fractional distillation. Often the only separation that is achieved is an aqueous phase containing mostly carbohydrate-derived compounds and an organic phase containing mostly lignin-derived compounds. The deconstructed biomass contains considerably more oxygen than does petroleum, which must be substantially removed if hydrocarbon fuels are desired.

8.6.1 Chemical Upgrading from the Perspective of Petroleum Refining

Differences between deconstructed lignocellulosic biomass and petroleum preclude its direct substitution into a conventional petroleum refinery. However, the basic refining processes of *cracking*, *treating*, *reforming*, *combining*, *and reshaping* still have relevance to upgrading of deconstructed biomass. Reactions in the presence of hydrogen, collectively referred to as *hydroprocessing*, are especially relevant because of their ability to deoxygenate biomass at high carbon utilization efficiencies. These include hydrotreating and hydrocracking. *Steam reforming* is also extremely important for its ability to generate the hydrogen required for hydroprocessing.

Basic refining processes are described in the following sections in terms of the kinds of chemical reactions that occur. These include *elimination reactions*, *substitution reactions*, *addition reactions*, *and rearrangement reactions* (refer to Chapter 3).

Cracking

Cracking, as defined in the petroleum industry, is *elimination reactions* that break the very large molecules of heavy gas oil (230–425°C boiling point) or distillation residual (>425°C boiling point) into lower boiling point molecules that are

more easily upgraded to fuels in subsequent refining processes. Several kinds of crackers have been developed, classified as thermal crackers, catalytic crackers, or hydrocrackers.

Thermal crackers use high temperatures around 500°C to promote rapid decomposition of large molecules without the aid of catalyst or the addition of hydrogen. *Elimination reactions* of these large molecules are accompanied by scission of carbon–carbon bonds and formation of carbon–hydrogen bonds, which results in a deficit of hydrogen and the formation of elemental solid carbon, known as coke. Addition of steam can reduce "coking," but not eliminate it. Furthermore, the reaction of steam and coke simply produces light gases rather than fuel-range molecules.

Catalytic cracking produces higher yields of fuel-range molecules, but there is still a deficit of hydrogen and coke deposits on the catalyst, eventually deactivating it. In a process known as fluid catalytic cracking (FCC), the catalyst is continuously circulated from the cracking reactor to a catalyst regenerator that burns off the coke and returns it to the cracking reactor. Interestingly, catalytic cracking with a zeolite catalyst is effective in deoxygenating deconstructed plant carbohydrates through the elimination reactions of decarbonylation (CO removal) and decarboxylation reactions (CO_2).

Hydrocracking is catalytic cracking in the presence of hydrogen, which allows more hydrocarbons and less coke to form. Hydrocracking would be particular effective in producing deoxygenated, fuel-range molecules from the phenolic oligomers in bio-oil. Although more carbon efficient than thermal or catalytic cracking, hydrocracking has the disadvantage of needing an external source of hydrogen, which adds to the expense of the process.

Treating

Treating has the goal of removing objectionable elements from the feedstock and stabilizing it for subsequent refining steps. The elements in question include nitrogen, sulfur, chlorine, and oxygen. They occur as both heteroatoms in carbon rings and as part of functional groups. They do not exceed more than a few weight percent in unrefined petroleum. Deconstructed lignocellulosic biomass also contains these elements but usually in smaller concentrations with the prominent exception of oxygen, which may represent 50 wt% of the dry feedstock. These elements are undesirable in the upgrading of feedstocks to hydrocarbon fuels, commonly interfering with catalytic upgrading or generating pollutant emissions when burned. In large concentrations, oxygen reduces the energy density and increases the molecular polarity of the fuel compared to hydrocarbons, which complicates their blending with petroleum-derived fuels.

Stabilization of the feedstock involves transforming particularly reactive molecules into forms more amenable to additional processing. In the case of

petroleum, the problematic hydrocarbons are the double carbon bonds of alkenes (also known as olefins), which can oligomerize in an undesired manner. In the case of deconstructed biomass, the functionality associated with aldehydes and carboxylic acids derived from carbohydrate and methoxy and vinyl substituents on phenolic compounds derived from lignin are thought to contribute to feedstock instability.

In a process known as hydrotreating in the petroleum industry, *substitution reactions* under relatively mild catalytic conditions replace sulfur, nitrogen, chlorine, and oxygen in the feedstock with hydrogen, yielding the respective byproducts hydrogen sulfide (H_2S), ammonia (NH_3), hydrochloric acid (HCl), and water (H_2O). Hydrotreating furthermore removes metal contaminants, which react with chlorine to form easily removed metal chlorides. *Addition reactions* of hydrogen also occur during hydrotreating of petroleum, saturating the double carbon bonds of alkenes in a process known as hydrogenation, improving the stability of the petroleum.

Applied to deconstructed biomass, hydrotreating removes nitrogen, sulfur, chlorine, and metals. It also hydrogenates vinyl functional groups. It would also partially deoxygenate the feedstock through *substitution reactions* with functional groups, but the reaction conditions are sufficiently mild that only the most reactive functional groups would be removed. More severe reaction conditions are required to completely deoxygenate the deconstructed biomass, such as previously described cracking.

Reforming

Reforming consists of a variety of *elimination reactions* that remove molecular hydrogen from hydrocarbons or other organic compounds. It may be thought of as the reverse of hydrogenation although reforming reactions can be more involved than simply producing unsaturated carbon–carbon bonds. Under high-temperature reforming conditions in the presence of steam, the ultimate products of reforming are CO and H_2, a circumstance that is exploited to convert natural gas or other sources of simple organic compounds into syngas. High-temperature reforming may be accomplished without a catalyst although catalysts are frequently employed for lower temperature reforming.

In the petroleum industry a process called catalytic reforming is employed to convert naphtha from the distillation of petroleum (220–315°C boiling point range) into gasoline molecules (90–220°C boiling point range). Among the most important reactions in catalytic reformers are *elimination reactions* that either convert alkanes (paraffins) into cycloalkanes (naphthenes) and hydrogen or cycloalkanes into aromatics and hydrogen. Not only are the hydrocarbon products higher octane fuel molecules than the reactants, the hydrogen is useful for hydrotreating and hydrocracking.

Catalytic reforming as practiced by the petroleum industry has little relevance to refining deconstructed biomass because it contains few hydrogen-rich molecules in the naphtha range. On the other hand, steam reforming light oxygenates (C_2–C_3) derived from carbohydrate, which would be difficult to upgrade into fuel-range molecules, produce large quantities of hydrogen for hydroprocessing.

Combining

Combining is *addition reactions* that convert two molecules into a single larger molecule. This is highly desirable from the standpoint of producing liquid fuels from biomass-derived molecules that otherwise are too volatile (C_2–C_4) to be used for fuel. A prominent example of addition reactions in petroleum refining is alkylation of isobutene (C_4H_{10}) with propene (C_3H_6) or butene (C_4H_8) to produce isoheptane (C_7H_{16}) and isooctane (C_8H_{18}), respectively, both important as gasoline-range molecules. *Addition reactions* also include polymerization (or more correctly oligomerization), which is the compounding of monomers into hydrocarbon chains. For example, the low-boiling point olefin monomers of propene and butene can undergo additive polymerization to produce high-octane, gasoline-range molecules known as polymer gasoline. Of course, if oligomerization proceeds too far, the molecular weights become too high for fuel applications (due to high viscosity and low volatility). Although deconstructed biomass is not rich in olefins, it contains other compounds that can easily polymerize, such as the phenolic monomers produced from lignin, but this usually occurs in an uncontrolled manner, producing molecules too large to use as transportation fuels.

Reshaping

Reshaping, or isomerization, is the rearrangement of chemical bonds among the constituents of a molecule to produce a molecule with the same chemical formula but distinctive chemical and physical properties. Isomerization is important in increasing the octane rating of fuels, especially by converting normal (straight-chain) alkanes into iso-alkanes (containing branched chains). In petroleum refining, some isomerization occurs in catalytic reformers. Dedicated isomerization plants are also built to produce feedstocks for alkylation plants and to improve the octane rating of straight-chain pentane and hexane. Isomerization would likely be important in a mature advanced biofuels industry. Currently the focus is on deoxygenating biomass-derived molecules into fuel-range hydrocarbons suitable for blending with petroleum-derived fuels rather than optimizing octane or cetane numbers.

8.6.2 Upgrading Deconstructed Lignocellulosic Biomass

The field of upgrading deconstructed lignocellulosic biomass into fuels is still developing, but some general strategies are emerging. Bio-oil from pyrolysis and

solvolysis would likely be upgraded in a similar manner, despite some important differences between them. The bio-oil from solvolysis consists of only the water-insoluble organic phase of the solvolysis products in contrast to bio-oil from pyrolysis, which is an emulsion of the water-insoluble organic phase in the aqueous phase. Solvolysis apparently deoxygenates biomass sufficiently to cause phase separation into separate water-insoluble and aqueous phases. Bio-oil can also be recovered as separate insoluble and aqueous phases, either by addition of water to the bio-oil or through the use of fractionating recovery processes during pyrolysis. In either case it appears that the water-insoluble phase is derived substantially from lignin while the aqueous phase is derived from the carbohydrate.

Early attempts to upgrade bio-oil focused on hydroprocessing to simultaneously remove oxygen and crack the large phenolic oligomers. The high temperatures employed quickly caused unstable functional groups, probably carbonyl in the carbohydrate-derived compounds and vinyl groups on phenolic compounds, to foul the catalysts with coke. Since then it has been discovered that mild hydrotreating of the bio-oil improves the stability of the bio-oil without substantially deoxygenating it. A second, more severe stage of hydrotreating then deoxygenates especially the light carbohydrate compounds, producing a product stream of light hydrocarbon oil, heavy phenolic oil, and light hydrocarbon gases. After separating these streams, the heavy phenolic oil is hydrocracked, which both reduces the phenolic oligomers to fuel-range molecules and deoxygenates functional groups and hydrogenates some of the aromatic rings. In principle, the heavy phenolic oil could be catalytically cracked, which would reduce hydrogen demand, but current zeolite catalysts do not appear efficient at cracking this material. The products of hydroprocessing are recovered as gasoline- and diesel-range molecules and light hydrocarbon gases that can be steam reformed to produce part of the hydrogen required for hydroprocessing with the balance coming from natural gas reforming. The overall process for upgrading whole bio-oil is illustrated in Figure 8.12a.

There are two major problems with upgrading whole bio-oil. First, not enough light hydrocarbon gases are generated to supply hydrogen via steam reforming. Natural gas is a relatively inexpensive source to supply the hydrogen deficit, but it is a fossil fuel and generates net greenhouse gas emissions. This deficit in hydrogen arises from the highly oxygenated nature of the aqueous phase of the bio-oil compared to the organic phase. Second, much of the organic content of the aqueous phase consists of C_2- and C_3-oxygenated molecules that consume significant hydrogen to deoxygenate them but yield molecules too small to be used in gasoline. They are simply recycled to the steam reformer, which represents inefficient uses of energy and hydrogen. A solution to these problems is illustrated in Figure 8.12b. The bio-oil is separated into water-insoluble organic phase and aqueous phase with the former upgraded through one or two stages of hydrotreating and one stage of hydrocracking, while the aqueous phase is steam reformed to hydrogen. The amount of hydrogen generated in this manner is more than required to upgrade the organic phase, thus avoiding the use of fossil fuels to produce the

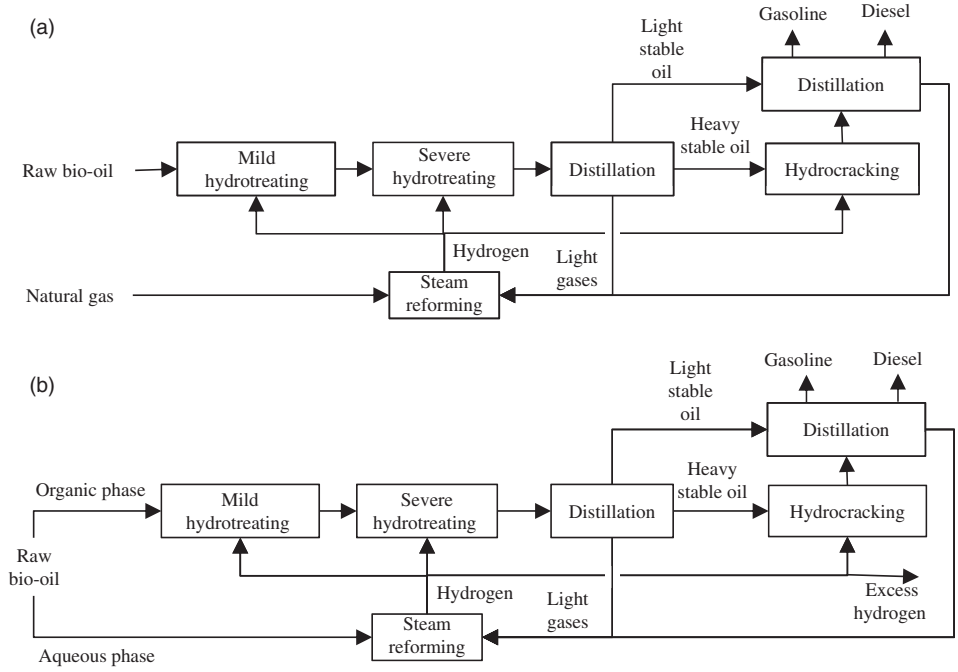

FIG. 8.12 Upgrading of pyrolysis liquids (a) hydroprocessing whole bio-oil; (b) hydroprocessing organic phase (aqueous phase steam reformed to hydrogen). Adapted from Jones, S.B., Valkenburg, C., Walton, C.W., et al. (2009) Production of gasoline and diesel from biomass via fast pyrolysis, hydrotreating and hydrocracking: a design case. *PNNL Report PNNL-18284*.

fuel. The process is not as carbon efficient in converting biomass to biofuels as upgrading whole bio-oil, but it has significantly lower greenhouse gas emissions.

Other approaches to improving the utilization of the aqueous phase for biofuels production is to increase the amount of carbohydrate converted to sugars or anhydrosugars, which would produce C_5 and C_6 hydrocarbons upon catalytic upgrading. This possibility was discussed in the section on pyrolysis. Another approach is to identify catalytic processes that build fuel-range molecules from C_2–C_4 molecules through *addition reactions* or *condensation reactions*. Various alkylation and aldol condensation reactions in combination with ketonization and dehydration reactions are being developed to convert these small molecules into C_7–C_{15} fuel molecules.

Further Reading

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CHAPTER

9

Processing of Oleaginous Biomass

9.1 Introduction

Oleaginous biomass includes traditional oil seed crops such as rapeseed and soybeans, unconventional crops such as jatropha and jojoba, aquatic species such as microalgae, and even animal manure and sewage. In some cases lipid content is high enough to justify its recovery through mechanical pressing or solvent extraction. When lipid is difficult to separate from biomass due to low concentration or challenging substrate or the lipid-rich remnant is to be utilized, other approaches are employed to recover energy from these feedstocks. These alternatives include hydrothermal processing and pyrolysis, which produce energy-rich organic liquids suitable for upgrading to liquid fuels, and anaerobic digestion to produce methane.

9.2 Lipids

Lipids were historically defined as compounds of biological origin that are soluble in organic solvents. Lipids include terpenes and esters of fatty acids. Terpenes include a large number of hydrocarbons that occur naturally in many plants, some of which have been significant sources of biobased products for thousands of years. Esters of fatty acids produced in plants and a variety of microorganisms include waxes and triglycerides. The energy-rich triglycerides, esters of glycerol and long-chain fatty acids, are of particular interest in the production of biobased products.

9.2.1 Triglycerides

Triglycerides, also known as fats and oils, are esters of glycerol and fatty acids. Recall that fatty acids are long-chain carboxylic acids containing even numbers of carbon atoms. The acid fractions of triglycerides can vary in chain length and degree of saturation. Fats, which are solid or semi-solid at room temperature, have a high percentage of saturated acids, whereas oils, which are liquid at room temperature,

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have a high percentage of unsaturated acids. Plant-derived triglycerides are typically oils containing unsaturated fatty acids, including oleic, linoleic, and linolenic acids.

9.2.2 Terpenes

Terpenes are any of various isomeric hydrocarbons $(C_5H_8)_n$, where n is 2 or more, originally derived from turpentine, an oleoresin obtained from coniferous trees. Terpenes, abundant in a variety of plants, are responsible for the odors of pine trees and the color of carrots and tomatoes.

Structurally, terpenes consist of two or more isoprene units joined together, which is called a conjugated diene, a compound containing two double bonds of carbon joined by one single bond. These compounds may have different degrees of unsaturation and a variety of functional groups. Terpenes range from relatively simple hydrocarbons to large polymeric molecules (polyisoprenes). Terpenes from conifers were the source of naval stores, the resinous substances used to maintain wooden ships and ropes. Polyisoprenes from the hevea rubber tree (*Hevea braziliensis*) or the guayule shrub (*Parthenium argentatum*) are the basis for natural rubber.

The hydrocarbon content of plants is a small fraction of the total plant material. Typical terpene content of mesophytic biomass species is only 0.5–1.5 wt%. Thus, economic recovery historically required tapping of living biomass, as is done with hevea rubber trees, or recovery as a coproduct in the processing of other biomass components, such as the production of turpentine as part of wood pulping. More recently, genetic engineering has been used to isolate genes for terpene biosynthesis and optimized its expression in yeast or bacteria, which can then be cultured in bioreactors with the goal of producing commercially significant quantities of hydrocarbons for fuels and other applications.

9.3 Lipid Extraction

Extraction of lipids from oil seeds is relatively straightforward. The seeds are crushed to release the oil from the seed. Mechanical pressing is used to extract oil from seeds with oil content exceeding about 20%. Solvent extraction is required for seeds of lower oil content. The residual seed material, known as meal, is used in animal feed.

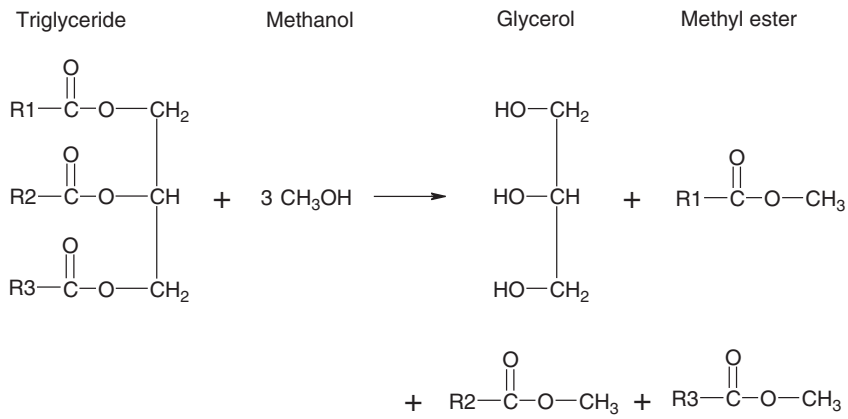
Extraction of lipid from microalgae is still under development. Lipids can be extracted from either dry algal biomass (10–15% moisture) or wet algal filter cake (80% moisture). Lipid extraction from dry algal biomass can be accomplished in a manner similar to lipid extraction from oil seeds, using either mechanical pressing or solvent extraction. Products include lipid and dry algal remnant. However, significant thermal energy is consumed in drying the algal biomass even when starting

with filter cake. Lipid extraction from wet filter cake is not well developed but is envisioned to include disrupting the cell wall (lysis) either through mechanical treatments such as ball milling and mixing with a solvent such as hexane to dissolve the lipids. The mixture is decanted to recover the solvent phase containing the lipids, an aqueous phase, and wet algal remnant. A multiple effect evaporator is used to separate the lipid from the hexane, which is recycled.

Triglycerides, in principal, can be directly used as fuel in diesel engines. However, their high viscosity results in frequent fouling of the injectors and rings in diesel engines. Triglycerides can be chemically modified to reduce their viscosity and improve their fuel properties. Most widely practiced today is transesterification of triglycerides to biodiesel although hydrotreating is likely to find wider application if plentiful sources of inexpensive lipids can be developed.

9.4 Transesterification of Triglycerides

Transesterification describes the process by which triglycerides are reacted with methanol or ethanol to produce methyl esters and ethyl esters, respectively, along with the coproduct glycerol. For example, one triglyceride molecule reacts with three methanol molecules to produce one molecule of 1,2,3-propanetriol (glycerol) and three ester molecules:



(9.1)

Near quantitative yields of methyl (or ethyl) esters can be produced in 1 hour at room temperature using 6:1 molar ratios of alcohol and oil when catalyzed by 1% lye (NaOH or KOH).

The lye also serves as a reactant in the conversion of esters into salts of fatty acids. These salts are familiarly known as soaps and the process is called saponification (soap forming). Small amounts of soap are also produced by the reaction of lye

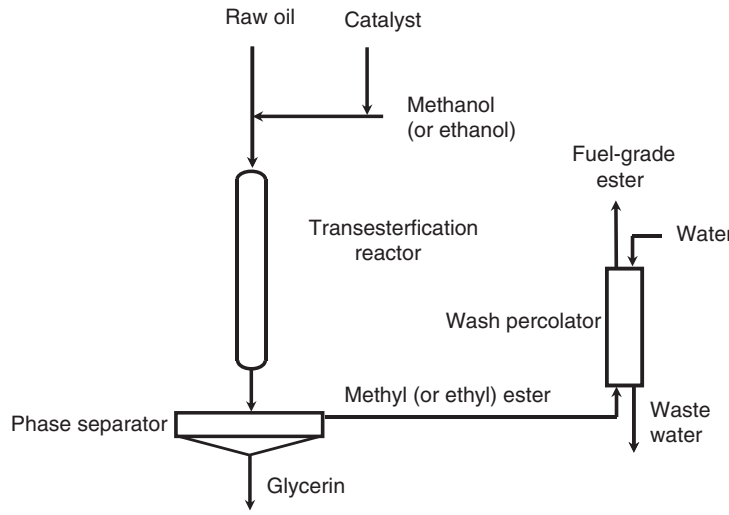


FIG. 9.1 Conversion of triglycerides to methyl (or ethyl) esters and glycerol.

with fatty acids. Upon completion, the glycerol and soap are removed in a phase separator. A flow sheet for a biodiesel production facility is given in Figure 9.1.

The name biodiesel comes from the fact that plant-derived methyl esters have combustion properties similar to the fuels designed for diesel engines. Nevertheless, biodiesel is chemically distinct from petroleum-derived diesel with the result it is not a perfect diesel fuel substitute. Like the lipids from which they are obtained, fatty acid methyl esters are subjected to microbial or oxidative attack, making them unsuitable in applications requiring long-term fuel storage. Low-temperature operability has occasionally been a problem. Whereas petroleum-derived diesel can be formulated from a broad range of hydrocarbons to give desired properties, the range of plant-derived triglycerides is more constrained for the production of biodiesel. Long-chain methyl esters and biodiesel contaminants such as sterol glycosides can solidify at low temperatures, causing fuel filters to plug. Other disadvantages of biodiesel are the consumption of fossil fuel–derived methanol in its manufacture and the generation of low-value glycerin as a major coproduct.

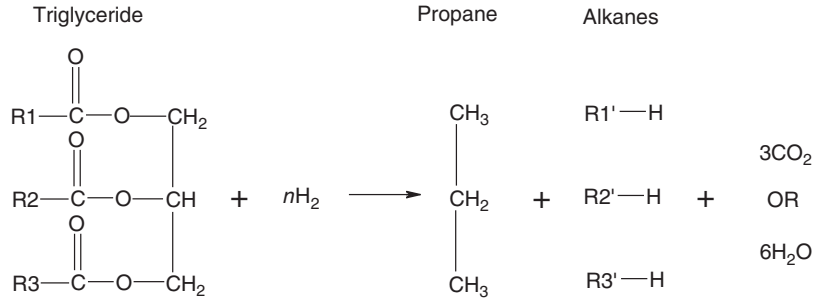
9.5 Catalytic Upgrading of Triglycerides

An alternative to transesterification of triglycerides to produce methyl ester and glycerin is catalytic upgrading to synthetic gasoline or diesel. If triglycerides are first pretreated to remove alkali metals and other contaminants, they can be mixed

with vacuum gas oil, one of the heavier cuts from vacuum distillation of petroleum, and cracked to gasoline range molecules in a fluidized catalytic cracker (FCC) in a petroleum refinery.

Alternatively, triglycerides can be hydrotreated to produce synthetic diesel in two steps. The first step removes alkali metal and other contaminants and saturates carbon–carbon double bonds in the fatty acid chains, which are responsible for the tendency of lipids to go rancid over time. By hydrogenating these to single bonds, the stability of the fuel is improved. The second hydrotreating step separates the fatty acids from the glycerin backbone of the triglycerides. It also removes the oxygen atoms responsible for the acidic nature of fatty acids, either by hydrodeoxygenation or decarboxylation (removal of oxygen as carbon dioxide), transforming these long-chain molecules into hydrocarbons. Furthermore, hydrogen reacts with the glycerol to form propane, a commercially important gaseous fuel.

The nature of the long-chain hydrocarbons formed from hydrotreating triglycerides depends upon the lipid feedstock. Rapeseed, for example, produces mostly hydrocarbon chains containing 16, 18, or 22 carbon molecules. Thus, these hydrocarbons can rightly be described as diesel fuel since petroleum-based diesel contains hydrocarbons containing between 10 and 22 carbon atoms (although there are some differences in the arrangement of these carbon atoms).



Hydrotreating vegetable oils and animal fat to produce synthetic diesel fuel has been demonstrated at large scale. The propane and other light hydrocarbons produced are used to generate hydrogen needed for hydrotreating. Wide scale commercial deployment awaits greater supplies of low-cost lipid feedstocks.

The use of refinery hydrotreaters presents important advantages over other approaches to advanced biofuels since it reduces the capital cost of biorefinery infrastructure and allows accelerated deployment of the technology if sufficient quantities of lipid feedstock can be procured. It also raises concerns among those who imagined lipid-based biofuels would always be the province of farmer-entrepreneurs. However, even the first generation of lipid-based manufacturing

plants have shifted over time from a few million gallons per year to several tens of millions of gallons capacity including a couple of plants in the United States of about 100 million gallons capacity. Economies of scale are as important to biorefineries as they are for petroleum refineries although the optimal sizes are likely to be quite different because of constraints in moving solid, low-density biomass to processing facilities.

9.6 Other Processing Options for Oleaginous Biomass

Although oleaginous biomass is rich in lipids, as shown in Figure 9.2, it also contains large amounts of other components including carbohydrate and protein. Soybeans contain 20 wt% lipids, but they also contain almost as much carbohydrate and twice as much protein. Even particularly lipid-rich strains of microalgae have more mass associated with the non-lipid components of their biomass. Simply extracting lipid from algal biomass and landfilling or land applying the remnant would be very wasteful of this biorenewable resource.

As shown in Figure 9.3, dry algal remnant could be pyrolyzed to bio-oil suitable for upgrading to transportation fuels. It could also be catalytic pyrolyzed to aromatic hydrocarbons. The wet algal remnant requires processes that are tolerant of high moisture feedstocks. Wet processing options include hydrothermal processing and anaerobic digestion. Although algal remnant mostly contains carbohydrate and protein, pyrolysis, hydrothermal processing, and anaerobic digestion are also able to convert lipid into value-added products. Thus, an alternative to extracting lipid and processing it separately from the algal remnant is to directly process the whole algal biomass. The following sections explore these possibilities.

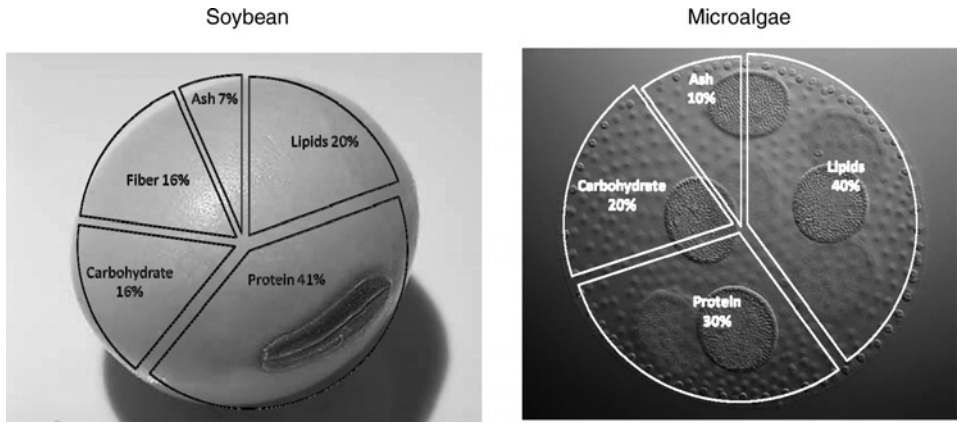


FIG. 9.2 Most kinds of oleaginous biomass are both lipid and protein rich.

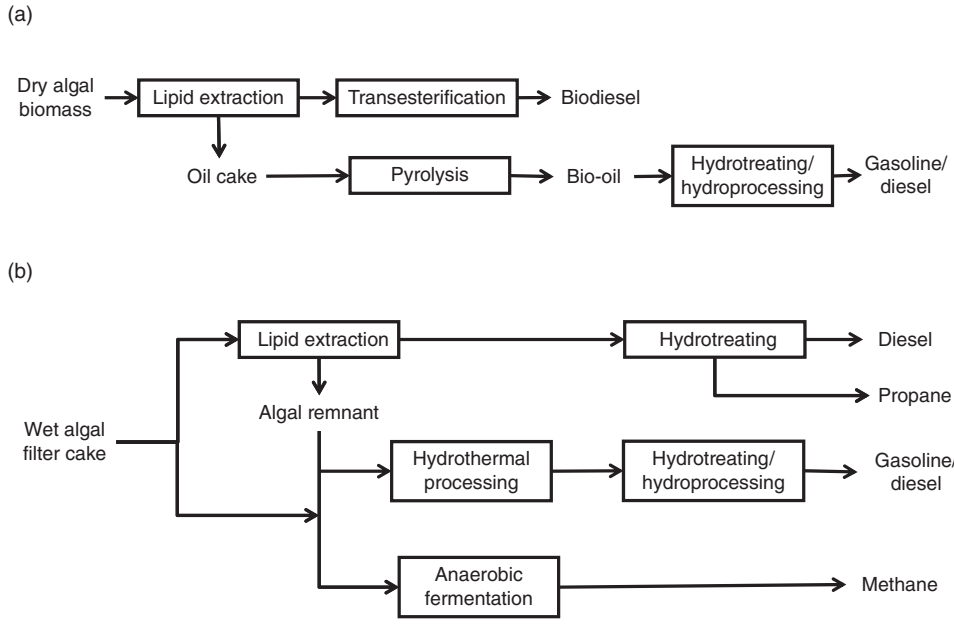


FIG. 9.3 Possible processing routes for algal biomass: (a) dry processing; (b) wet processing.

9.6.1 Pyrolysis of Lipid-Rich Biomass

Pyrolysis is able to convert either whole algal biomass or algal remnant into a liquid product similar to the bio-oil produced from lignocellulosic biomass, as described in Chapter 8, but there are important differences. Because neither algal biomass nor algal remnant contains lignin, the oil does not contain the phenolic oligomers found in the bio-oil from lignocellulosic biomass. Lipids are converted into fatty acids or even alkanes, which are desirable from the standpoint of upgrading bio-oil. However, the protein in algal biomass and remnant are converted in part to a variety of nitrogenous compounds including pyrroles, nitriles, indoles, pyridines, and poly-heteroaromatic compounds. These molecules would have to be removed (by hydrotreating) to prevent them from poisoning upgrading catalysts or producing unacceptable nitrogen oxide emissions during combustion.

On the other hand, if algal biomass or remnants are pyrolyzed in the presence of a zeolite catalyst, the biomass is both denitrified and deoxygenated to produce aromatic hydrocarbons as the only major condensable organic compounds. Most of the nitrogen is converted to ammonia, a valuable fertilizer, or sequestered in the coke product. The aromatics, which are mostly benzene, toluene, and xylene, are high-value commodity chemicals and important blendstocks for enhancing the

octane rating of gasoline. The process is still under development but offers the prospect of directly converting algal biomass or remnant into high-value chemicals and fuels.

9.6.2 Hydrothermal Processing of Oleaginous Biomass

Hydrothermal processing, as described in Chapter 8, is a form of solvolysis with water serving as the solvent. Accordingly, it is extremely attractive for processing high moisture feedstocks like manure or microalgae, eliminating feedstock drying prior to thermochemical processing. Although the discussion of hydrothermal processing in Chapter 8 focused on lignocellulosic biomass, in many ways it has even better prospects for processing oleaginous feedstocks.

Carbohydrate in microalgae, because it is not embedded in a matrix of lignin, is more readily hydrolyzed to monosaccharides than the carbohydrate in lignocellulosic biomass. Lipids readily hydrolyze to fatty acids and glycerol at 250°C and 5 MPa. The free fatty acids, in turn, can be decarboxylated to form long-chain hydrocarbons especially in the presence of a base catalyst. Protein hydrolyzes to amino acids at relatively mild hydrothermal conditions (around 250°C) although yields are rarely more than 10–15 wt% since the amino acids subsequently decompose. However, hydrothermal processing of biomass is frequently conducted at more severe conditions with the goal of producing a mixture of organic compounds. As Figure 9.4 illustrates, liquefaction of oleaginous biomass produces a water insoluble biocrude, an aqueous phase, a residue that includes char, and gas. The biocrude resembles bio-oil except that it contains less water, is less oxygenated, and

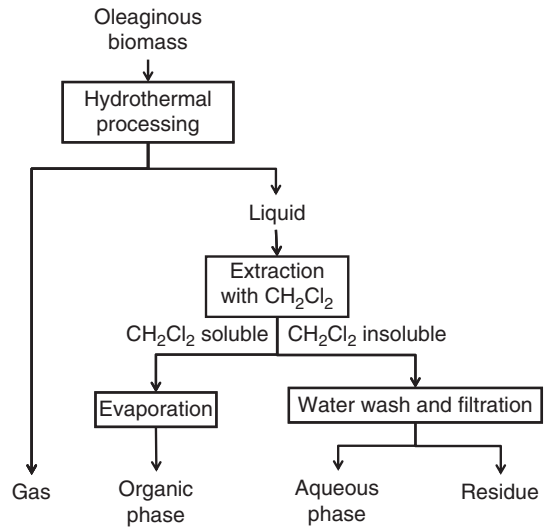


FIG. 9.4 Liquefaction of oleaginous biomass through hydrothermal processing.

is more viscous. Like bio-oil, it can be hydrotreated and hydrocracked to gasoline and diesel.

9.6.3 Anaerobic Digestion of Oleaginous Biomass

Biomass grown in aqueous environments presents special challenges to lipid recovery. Microalgae especially thrive under low population densities. High yields of oil are made possible by continuously harvesting low-density suspensions of microalgae from their aqueous environment. Dewatering these low-density suspensions requires a 500-fold concentration of the microbial biomass, which represents one of the major challenges in the production of algae-based fuels.

An alternative to directly harvesting the algae is to anaerobically digest them into a more easily recoverable fuel. Anaerobic digestion is the decomposition of organic matter, including polysaccharides, proteins, and lipids, into simpler compounds by bacteria in an oxygen-free, aqueous environment. It is widely used to treat municipal solid waste (MSW), municipal and industrial wastewater, and increasingly animal manure for the purposes of pollution control. The process occurs in stages, each involving specific types of bacteria, to successively break down the organic matter into simpler organic compounds. Complete digestion produces biogas, a gaseous mixture of CH_4, CO_2, and some trace gases, and a solid residue known as sludge.

Anaerobic digestion arises naturally in marshy ground and landfills. The English gave the name "will-o'-the-wisp" to the mysterious, ephemeral flames that appeared spontaneously in marshlands as a result of decaying vegetation. The origin of this flammable gas was recognized by the middle of the seventeenth century but not exploited until the end of the following century when gas from sewage was used for street lighting in England and power in India. These early systems were difficult to operate and maintain, and hydrogen sulfide in the gas corroded pipes and engines. Today, the technology is well developed for production of methane-rich gas from almost any kind of feedstock with the possible exception of lignins and keratins.

Fundamentals of Anaerobic Digestion

The complete anaerobic degradation of organic matter is a three-stage process. As illustrated in Figure 9.5, diverse bacterial consortia are involved in the hydrolysis, fermentation, acidification, and methanogenesis of the various components of biomass. The first step involves hydrolysis of polysaccharides to oligosaccharides and monosaccharides, of proteins to peptides and amino acids, of triglycerides to fatty acids and glycerol, and of nucleic acids to heterocyclic nitrogen compounds, ribose, and inorganic phosphate. Hydrogen and carbon dioxide are also produced. Coliform bacteria, such as the pathogen *Escherichia coli* and pathogens in the genera *Salmonella* and *Shigella*, are common fermentative bacteria.

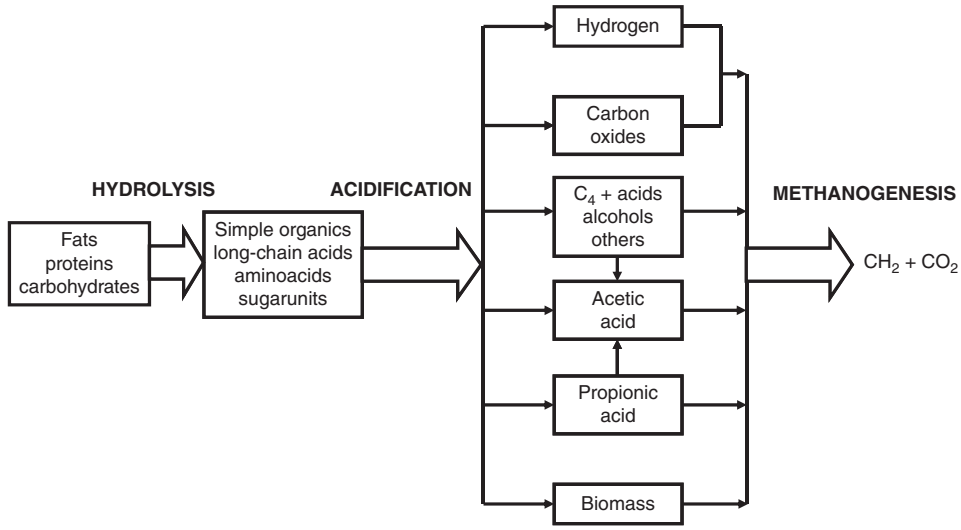


FIG. 9.5 Microbial phases in anaerobic digestion. Adapted from Klass, D.L. (1998) *Biomass for Renewable Energy, Fuels, and Chemicals*. San Diego: Academic Press.

This step is followed by transitional digestion through the action of acetogenic (acid-forming) bacteria. Products of fermentation that are too complex for methanogenic (methane-forming) bacteria to consume are further degraded in this step to acetate, H_2, and CO_2. Traces of oxygen in the feedstock are consumed in this step, which benefits oxygen-sensitive, methanogenic bacteria. Furthermore, nutrients such as ammonium salts from degradation of proteins are released. The final step, methanogenesis, converts acetate to CH_4 and CO_2 by the action of methanogenic bacteria. Furthermore, H_2 and CO2 released during acetogenesis are converted to additional methane. About 70% of the methane and carbon dioxide is produced from acetate and 30% is produced from carbon dioxide and hydrogen. The methanogenic bacteria lower the acidity of the fermentation broth, which is beneficial to acetogenesis since the acid-producing organisms are sensitive to high acidity.

Advantages of anaerobic digestion for processing biomass include the use of non-sterile reaction vessels; automatic product separation by outgassing; and relatively simple equipment and operations. The primary disadvantages are slow reaction rates and low methane yields. The breakdown of cellulose to sugars may require reaction times as long as a month to achieve high yields of methane. Some plant components are resistant to microbial degradation. Lignin, in particular, is only slowly converted because of its stable polyaromatic structure. Although the theoretical weight yield of methane from glucose is 27 wt%, the complex of lignin and cellulose known as lignocellulose in plant materials results in substantially

Table 9.1 Anaerobic digestion yields of biogas for various feedstocks

Feedstock	Biogas Yield (m^3/kg of Volatile Solids)
Wastewater	0.094–0.31
Human sewage	0.37–0.94
Distillery waste	>0.69

Source: Wyman, C.E. (1994) Alternative fuels from biomass and their impact on carbon dioxide accumulation. *Applied Biochemistry and Biotechnology*, 45/46, 897–915.

lower yields of methane than might otherwise be expected from cellulose. Another disadvantage is microbial reduction of sulfate and other sulfur compounds to hydrogen sulfide, a toxic, corrosive gas that complicates the use of biogas.

Anaerobic Digestion Equipment

All anaerobic digesters produce two effluent streams: biogas and sludge. Most digestion systems produce biogas that is between 55% and 75% methane by volume with the balance being carbon dioxide along with traces of hydrogen sulfide. The amount of biogas produced depends on both the composition of the feedstock and the design of the digester. Table 9.1 gives the range of gas yields expected for various feedstocks in terms of the volatile solids content of the material. Volatile solids are defined as the weight loss from a dried solids sample after firing in a muffle furnace at 550°C.

Anaerobic digesters can be broadly characterized as single-tank or two-tank reactors (also known as conventional or two-phase reactors, respectively). The single-tank reactors, illustrated in Figure 9.6, can be operated in one of the several modes: batch, intermittent, or continuous.

In the batch mode, the reactor is loaded with feedstock only once and microbial reactions are allowed to proceed to completion. Only gas is removed during the process. Batch reactors are inherently non-steady in their operation, which prevents optimum feedstock throughput and biogas yields. Thus, they are relegated only to the smallest digester systems.

The intermittent mode periodically adds additional feedstock as aqueous slurry while drawing off an equal volume of fermenter broth. Stratification occurs within the reactor, consisting of an active layer of digesting solids, an inactive layer of stabilized (indigestible) solids at the bottom, and a supernatant layer at the top. The surface of the supernatant layer is usually covered with a thin layer of scum. The challenge of this mode is retaining the sludge until it is fully digested. One way to improve efficiency is to encourage movement of feedstock through the active biosolids where the microorganisms reside. The intermittent mode requires retention times of 30–60 days and has loading rates of 0.5–1.5 kg per day of volatile solids per cubic meter capacity.

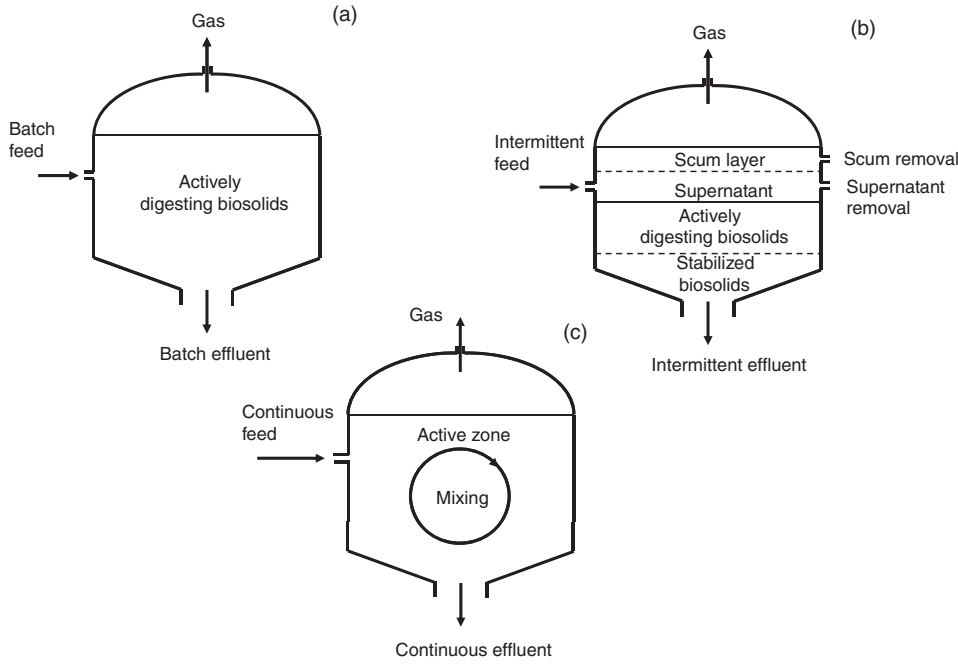


FIG. 9.6 Types of anaerobic digesters: (a) batch fed; (b) intermittently fed; (c) continuously stirred and fed.

Higher rate digestion can be achieved in continuous mode operation of single-tank reactors. Mixing is used to provide homogeneity. Retention times are 20 days or less and loading rates are 1.6–6.4 kg per day of volatile solids per cubic meter capacity.

Two-tank reactors, illustrated in Figure 9.7, were developed in response to the observation that methanogenesis appears to be the rate-limiting step in anaerobic

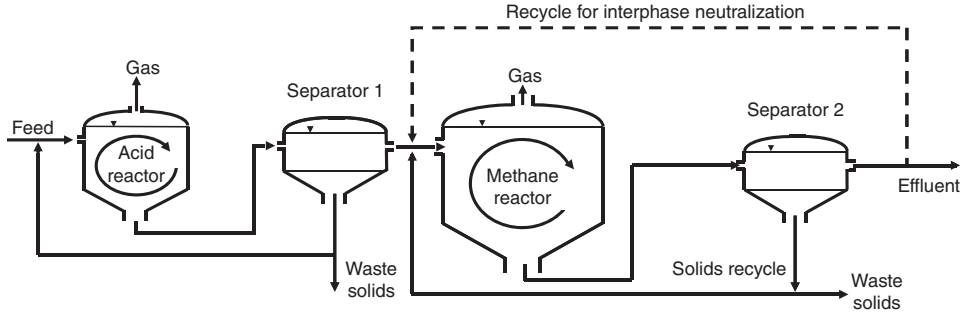


FIG. 9.7 Two-phase anaerobic digesters.

digestion. Two-tank reactors physically separate the acid formation and methane formation phases of digestion so that each takes place under optimal conditions. Benefits of this technology are numerous: hydrolysis and acidification occur more quickly than in conventional systems; the common problems of foaming in single-tank systems are reduced by the destruction of biochemical foaming agents before they reach the methane-forming reactor; and the biogas produced is typically rich in methane.

The biological conversion process of anaerobic digestion can be used for a wide range of feedstocks of medium-to-high moisture content. Sewage sludge is most commonly used as feedstock for anaerobic digesters, but MSW, food processing wastes, agricultural wastes, Napier grass, kelp, bagasse, and water hyacinth can also be digested. Digesters are designed to maintain optimal conditions for a specific type of waste. Waste pretreatment, heating, mixing, nutrient addition, specialized bacteria addition, and pH adjustment can be manipulated to control digester performance.

Biogas, once treated to remove hydrogen sulfide, can substitute for natural gas in many applications, including stationary power generation. The carbon dioxide can be recovered and sold, and the digested solids are often marketable as fertilizer, animal bedding, and sometimes as animal feed. The digested solids have higher nutrient values per unit mass than the undigested feed solids and are effectively slow-nitrogen-release fertilizers.

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CHAPTER
10

Processing of Biorenewable Resources into Natural Fibers

10.1 Introduction

Plant fibers are long, hollow cells that provide structural support and/or conduct water and nutrients through the plant. The cell walls of fibers consist primarily of lignocellulose. Whereas the previous chapter considered how to depolymerize this material into simple molecular building blocks, this chapter is devoted to the processes that liberate fibers for the manufacture of biocomposites, paper, and other cellulose-based products.

The disintegration of plant material to recover fibers is known as pulping, a process that can be accomplished mechanically or chemically. Mechanical pulping, which physically separates the lignocellulosic fibers from one another, has yields of 91–98%. Mechanical pulp, which produces smooth printing surfaces of good opacity, has traditionally been employed in production of newsprint. Mechanical pulp usually needs to be supplemented with chemical pulp, about 5%, to provide the prerequisite strength required to survive modern high-speed printing presses.

Chemical pulping dissolves lignin, which serves as an adhesive in cell walls, thus liberating cellulosic fibers. The advantage of chemical pulping is the production of cellulosic fibers, which are an order of magnitude stronger than the lignocellulosic fibers produced by mechanical pulping. However, it also dissolves hemicellulose, with the result that chemical pulping yields are only 35–60%. Chemical pulping is used for the production of paper for packing, writing, hygienic products, and for cellulose derivatives. Chemical pulping accounts for 70% of the total worldwide production of pulp.

In principle, both woody and herbaceous plant materials can be used for the production of pulp. Indeed, agricultural residues were a major source of pulp in the United States and Europe until the 1920s when issues of quality and supply began to favor woody biomass. Today, more than 90% of pulp and paper is produced from woody biomass.

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Although the lengths of fibers from herbaceous materials are comparable to those in hardwoods, they are typically shorter than the fibers obtained from softwoods; thus, paper made from herbaceous plant fibers has relatively low tear strength, an undesirable characteristic for many applications. Herbaceous materials also contain about 30 wt% of pith or parenchyma cells and about 5 wt% of dense epidermis material, neither of which is fibrous in nature. When left in the pulp, they have deleterious effects on paper quality.

Another factor, possibly even more important to the demise of herbaceous biomass pulping, was increased labor costs associated with securing supplies of agricultural residues. These materials have very low bulk density, resulting in tremendous volumes to handle, and they rapidly degrade when exposed to the weather, requiring special provisions for long-term storage.

Depithing processes, described in a subsequent section, can substantially overcome many of the fiber quality issues while modern methods of collecting, storing, and handling herbaceous biomass, previously described in Chapter 5, should help overcome supply problems. Certainly, a substantial volume of agricultural residues goes unused in the world today.

The following sections describe various aspects of fiber processing including mechanical pulping, chemical pulping, and depithing operations.

10.2 Mechanical Pulping

Germany introduced groundwood pulping in 1840 as a source of fibers to replace increasingly scarce rags for the production of paper. In this process, wood is mechanically ground by large stones. The pulp is then screened to remove knots and other large pieces of wood followed by washing and bleaching in preparation for papermaking. Thermomechanical pulping was developed in the 1930s. In this process, wood chips are ground under pressure, producing heat that weakens the lignin in the wood chips, making the separation of fibers easier. Thermomechanical processing yields relatively cheap fibers suitable for newsprint. Refiner mechanical pulping was developed in the 1960s. Wood chips are passed repeatedly through a series of rotating discs to remove fibers.

Although mechanical pulping provides high yields of fiber, it is energy intensive and does not remove lignin, which degrades paper strength and is responsible for darkening of newsprint with time.

10.3 Chemical Pulping

The two principal chemical pulping processes are the sulfite process and the sulfate process, also known as the kraft process. Until recently, the sulfite process was

preferred because it produced a much lighter, easier to bleach pulp. However, the environmental impact of the sulfite process is greater than the kraft process, which has well-established methods for recovering processing chemicals and utilizing lignin that would otherwise be discharged to the environment. Since the 1950s, the kraft process has gradually replaced the sulfite process and today accounts for over 80% of chemical pulp. Nevertheless, the sulfite process presents some useful lessons in co-product utilization that will be described here.

10.3.1 Sulfite Pulping

The sulfite process is illustrated in the flow chart of Figure 10.1. The sulfite pulping liquor is an acid solution of bisulfite of calcium, magnesium, sodium, or ammonia, which is added to wood chips in a digester operated at 160°C. In about 2 hours, the lignin is sulfonated and the salts of the sulfonic acid are dissolved. Hemicellulose is hydrolyzed to pentoses and hexoses, depending on the chemical composition of the hemicellulose. The backbone of hemicellulose from hardwoods and herbaceous materials is primarily xylan, which yields xylose upon hydrolysis. The hemicellulose from softwoods is predominately mannan, which yields mannose, an epimer of glucose, upon hydrolysis. In addition, the liquor from pulping hardwood contains almost twice as much acetic acid as the liquor

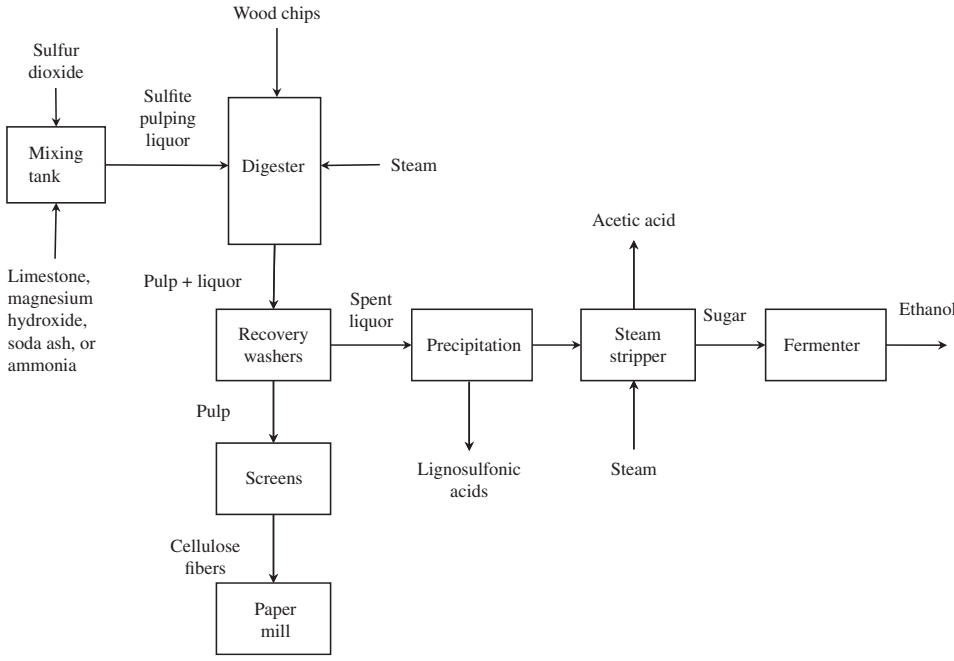

FIG. 10.1 Flow chart of sulfite pulping.

from pulping softwood due to higher acetyl content of hardwood hemicellulose. The sulfite process has not been generally employed for herbaceous fibers because of inferior yields and fiber strengths compared to the kraft process.

The pulp of cellulosic fibers is filtered from the spent liquor and then further processed to paper or cellulose derivatives. The spent liquor contains carbohydrates and lignin as well as pulping chemicals that should be treated as byproducts rather than waste streams discharged to the environment. The sulfonic acids of lignin, which are highly condensed, high molecular weight compounds, can be precipitated from the spent liquor and sold as a binder in the preparation of fertilizers, animal feed, and fuel pellets, as a glue substitute and drilling mud additive, and as a phenol substitute in the preparation of phenol–formaldehyde resins. Oxidation of lignosulfonic acids by air in strongly alkaline solution yields vanillin, a common flavoring agent and the raw material for the production of L-dopa, a pharmaceutical used for the treatment of Parkinson's disease.

Until recently, it was common to ferment the hexoses in spent liquor from softwood pulping to ethanol. Although phenol from lignin fragments inhibits fermentation, yeast was adapted to tolerate their presence in spent pulping liquor. Scandinavian pulping mills, in particular, generated ethanol for use as a 25% blend with gasoline although the practice was phased out in 1958. Fermentation of spent liquor from hardwood pulping was not widely practiced for two reasons: the high acetic acid concentrations are toxic to most microorganisms and xylose, the predominant sugar, is not readily fermented by common yeast. Steam stripping can reduce acetic acid to less than 0.5 g/L, an acceptable level for fermentation. In recent years, good progress has been made in identifying and developing pentose-fermenting microorganisms. Alternatively, the xylose could be dehydrated to furfural, as described in Chapter 6.

10.3.2 Kraft Pulping

Kraft pulping was developed in Germany near the end of the nineteenth century in an effort to improve upon an early pulping process known as the soda process or alkaline pulping, which used sodium hydroxide (NaOH) to pulp wood. The soda process could not compete with the sulfite process due to the relatively high cost of NaOH. The key innovation in kraft pulping was the replacement of sodium carbonate as make-up chemical with inexpensive sodium sulfate (Na_2SO_4). Upon heating, Na_2SO_4 is converted to sodium sulfide, which reacts with water to form NaOH and sodium hydrosulfide (NaSH). The process produced a strong pulp, which was the source of its name, kraft being the German word for "strong." It is also known as the sulfate process for the compound used as make-up chemical. The kraft process was quickly adopted in the United States, where it allowed commercial pulping of southern pines, which do not fare well in the sulfite process due to their high resin content.

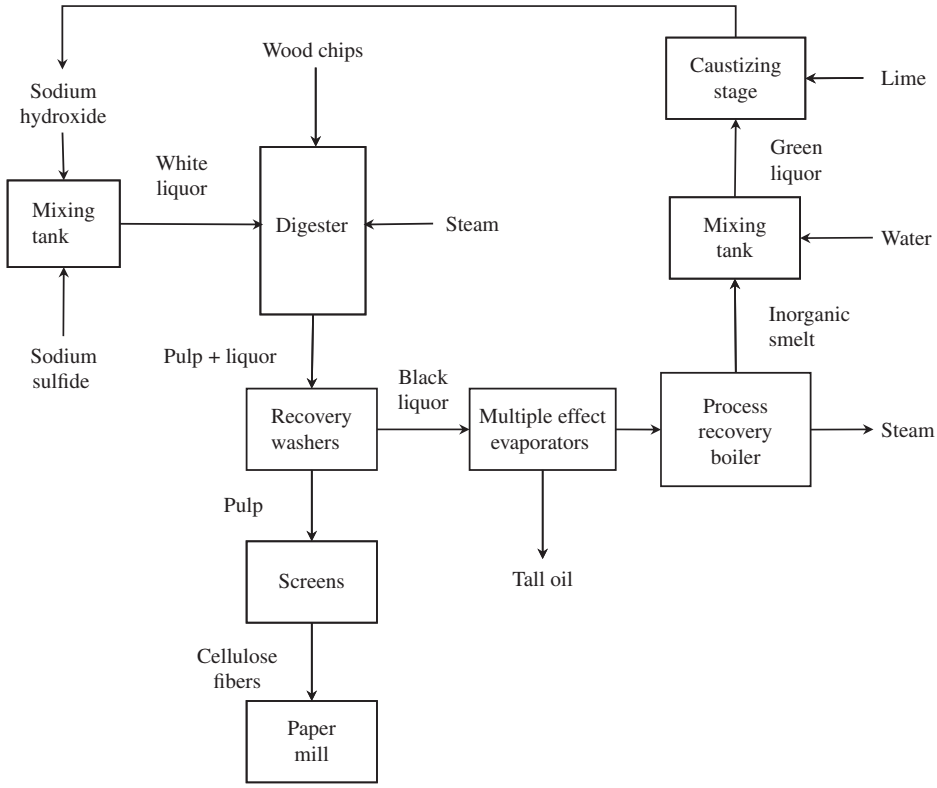

FIG. 10.2 Flow chart of kraft pulping.

The kraft process is illustrated in the flow chart of Figure 10.2. Biomass is first steamed before being continuously added to a digester. Pulping is performed with a hot mixture of NaOH and sodium sulfide (Na_2S) known as "white liquor." Roughly half of the biomass is degraded and dissolved to form a mixture of lignin, polysaccharides, and a small fraction of extractives. A substantial amount of the hemicellulose fraction of the wood is converted to hydroxy carboxylic acids. The lignin is degraded to a complex mixture of compounds. The soluble fraction is known as "kraft lignin" but has little resemblance to the native lignin in the wood.

The pulp of cellulosic fibers is washed to remove the spent liquor, which is known as "black liquor," and screened to remove knots. Additional processing of the pulp may include oxygen delignification to further remove lignin binding together with fibers and bleaching to brighten the fibers.

The black liquor is concentrated to 65–80% solids content with multiple-effect evaporators. Extractives present in the raw biomass and liberated during pulping can be removed during this stage. This so-called "tall oil" is comprised of soaps

formed from the saponification of fatty acid glycerides and the esters of resin acids, especially from the pulping of softwoods. Acidification of these soaps yields "crude tall oil," which contains 35% resin acids, 30% fatty acids, and 35% unsaponifiable terpenes and terpenoids, the latter resembling terpene hydrocarbons but with various oxygenated functional groups attached.

The black liquor also contains degraded polysaccharides and lignin. The polymeric lignin fraction can be precipitated by acidification although kraft lignin has only limited applications compared to the lignosulfonates obtained from sulfite pulping. Acid-precipitated kraft lignin had been used as an adhesive in panel boards. More generally, it has been employed as boiler fuel because of its high heating value compared to raw wood. The degraded polysaccharides are typically used as boiler fuel, too, although their relatively low heating value suggests that higher value applications should be explored.

The black liquor, containing degraded polysaccharides and lignin, is burned in a process recovery boiler, which generates steam and recovers pulping chemicals. Combustion of black liquor produces an inorganic smelt of sodium carbonate (Na_2CO_3) and Na_2S with a small amount of sodium sulfate (Na_2SO_4). The smelt is dissolved in water to form "green liquor," which is reacted in the causticizing stage with lime (CaO) to convert Na_2CO_3 into NaOH and regenerate the original white liquor. Due to incomplete reaction in the recovery cycle, the white liquor also contains Na_2CO_3 and sodium salts of oxidized sulfur-containing anions. The use of the process recovery boiler is integral to economic operation of a kraft pulping mill.

Herbaceous materials obtained from agricultural residues, including wheat and rice straw and bagasse from processed sugarcane, have relatively low lignin content, often only one-half that of woody material. Thus, chemicals more easily penetrate plant cell walls, and pulping of herbaceous materials may be accomplished in only one-fourth to one-third the time required for woody materials. In fact, pulping is so rapid that there is no advantage in using sodium sulfide as part of the white liquor prepared for the kraft pulping process. Instead, the simpler soda process, using only sodium hydroxide, is often used to pulp herbaceous biomass.

Complicating the pulping of agricultural residues are the large quantities of ash, particularly silica, compared to woody materials. This silica appears in the black liquor of kraft or soda processes, where it creates severe problems in recovery operations, especially in the formation of silica scale on heat transfer surfaces of evaporators and boilers.

Desilication of the black liquor can be accomplished with either lime treatment or by pH adjustment. Lime precipitates silica as calcium silicates by the reaction:

$$Na_2SiO_3 + CaO + H_2O \rightarrow CaSiO_3 + 2NaOH \tag{10.1}$$

The calcium silicate precipitates from the solution and is removed by filtration. Because this reaction also precipitates out sodium carbonate and sodium sulfate,

pH adjustment by passing carbon dioxide in the form of flue gas through the black liquor is considered the best approach to desilication. This approach precipitates silicon dioxide, which is removed by band filters. Alkali consumption is economized by vacuum stripping the carbon dioxide from the desilicated liquor, which decomposes the bicarbonates formed.

10.4 Depithing

The stalks of some herbaceous plants, such as sugarcane and corn, contain 25–35% on a dry weight basis of parenchyma cells (pith), which do not have the characteristics of fiber. Pith, containing a high portion of hemicellulose, is readily penetrated and reacted by pulping chemicals; thus, pith consumes a large fraction of the chemicals while yielding little useable pulp. Furthermore, the outer surface of these stalks consists of tough, waxy epidermis cells that are resistant to pulping chemicals. Representing about 5% of the dry weight of stalks, epidermis cells leave troublesome residues in the finished pulp, usually appearing as dark specks. Depithing is the process of removing parenchyma cells from herbaceous plant stalks. Many types of depithing operations also remove epidermis cells, producing a pulp suitable for paper products that do not require high tear strengths.

Sugarcane bagasse, the fibrous stalk residue remaining after pressing the cane for sugar, has been widely explored as a source of pulped fibers. The following depithing operations were developed for bagasse although they could equally apply to other herbaceous plant stalks.

Approximately 50% of the dry weight of bagasse stalks consists of high-quality fiber bundles concentrated in the hard, dense rind of the stalk. These fiber bundles are separated relatively easily from the pith tissue in which they are embedded. An additional 15% of the stalks are shorter, less resistant fiber bundles scattered throughout the interior pith portion. These bundles are more easily dissociated into individual fibers than those found in the rind. Separation of these two kinds of fibers during depithing operations is not generally considered economical.

Depithing can be classified into three categories: dry depithing, moist depithing, and wet depithing. Dry depithing separates the pith from bagasse after it has been dried to 10–25% moisture content. Although widely used prior to 1960, the method was inadequate for production of high quality pulp. Other depithing methods are more appropriate for modern storage and processing of bagasse. Moist or humid depithing employs bagasse "as received" from a sugar mill, which usually has moisture content of 50%. This operation is the most economical of the three but does not achieve fibers as clean and uniform as can be obtained by wet depithing. The third type of depithing operation employs a slurry of water and bagasse to improve depithing. Wet depithing also has the advantage of removing epidermis cells as well as pith if stalks are well broken up in the milling process.

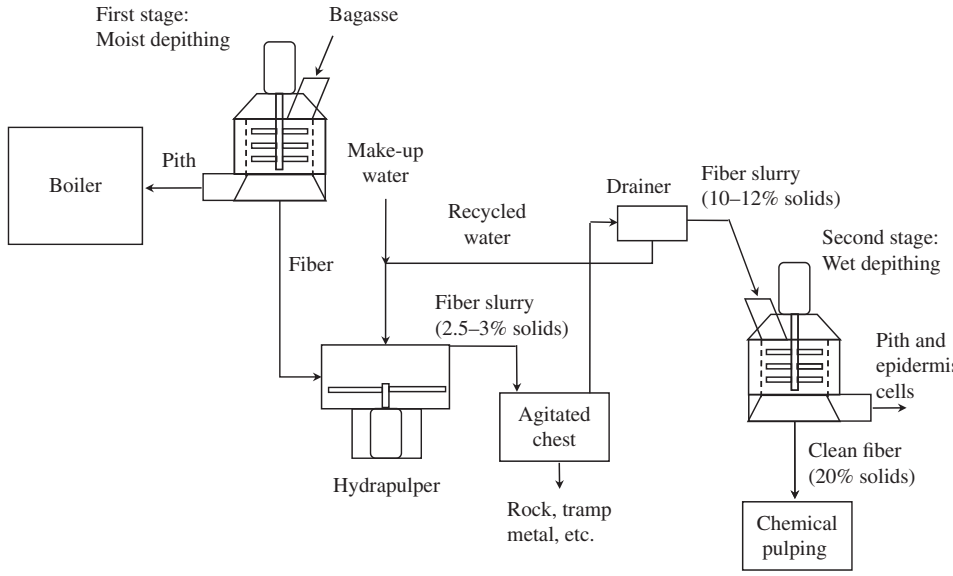

FIG. 10.3 Flow chart of two-stage depithing operation.

However, wet depithing of raw bagasse generates a large amount of wet pith, which is difficult to handle.

Many commercial operations employ a two-stage depithing operation consisting of moist depithing, which economically removes most of the pith, followed by wet depithing, which removes the residual pith as well as epidermal cells from the fiber. An example of such a two-stage operation is illustrated in Figure 10.3. As-received bagasse is fed to a depithing machine consisting of a rotor to which are attached swinging or rigid hammers. The mechanical action rubs or breaks loose the pith from the fiber, which is flung radially outward through screens or perforated plates enclosing the rotor. Fibers, which are too large to pass through the screens, fall downward where they are separately collected. If this process is performed at the sugar mill, the pith removed, representing 30–40% of the weight of bagasse, can be employed as fuel in the mill's boiler. The cost of transporting the resulting fiber to a pulping mill is substantially less than for the raw bagasse.

The second stage of depithing occurs at the pulping mill. Bagasse and water are continuously added to a "hydrapulper," which thoroughly wets the bagasse and helps break loose dirt and pith. The resulting slurry, which contains 2.5–3% solids, is pumped to agitated chests where rock, tramp metal, and other heavy material settle out. Since wet depithing machines are designed to operate with slurry of 10–12% solids content, the slurry passes through a dewatering device such as rotary drum, vibrating screen, drag drainer conveyor, or a screw-type drainer conveyor.

The drainers remove a considerable amount of dirt and some pith cells from the slurry, which is then pumped to the wet depither. The wet depithing machine, like moist depithing machines, consists of hammers attached to a rotor enclosed within a perforated drum. Pith and epidermal cells are small enough to pass through perforations, while the clean fiber slurry, with solids loading increased to about 20%, flows out the bottom. A screw feeder conveys the fiber slurry to the chemical pulping digester. The wet pith leaving the machine has solids content of only about 1%. Some places in the world use this waste stream to irrigate cane fields. Otherwise, wet pith must be dewatered to at least 15% for landfill or close to 50% for use as boiler fuel.

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CHAPTER
11

Environmental Impact of the Bioeconomy

11.1 Introduction

Much has been made of the negative environmental impact of using fossil fuels. The assumption has often been made that anything that reduces use of fossil fuels will therefore benefit the environment. The reality is much more complicated—every technology introduces both benefits and costs whose net impact depends upon what is most valued by society. Exploitation of biorenewable resources is no exception. Agriculture has been blamed for desertification in Africa while demand for fuel wood was clearly responsible for deforestation of large parts of Europe.

This chapter explores some of the potential environmental impacts of using biorenewable resources in the production of fuels, chemicals, energy, and fibers. These impacts are not always readily apparent; for example, the role of chlorofluorocarbons, once commonly used as refrigerants and blowing agents, in atmospheric ozone depletion was not recognized until decades after their commercial development. Thus, there is a tendency to err on the side of caution in assessing the potential negative impacts of new technologies on the environment. This chapter organizes the topic in terms of the broad areas of plant science, crop production, processing, and utilization of biobased products.

11.2 Plant Science

The potential impact of plant science on the environment is among the most contentious debates in modern society. The prospect of creating new plants by the application of biotechnology and releasing them to the biosphere or introducing them to the human food supply concerns many people. Particularly in Western nations, whose people enjoy secure food supplies and have the leisure and financial

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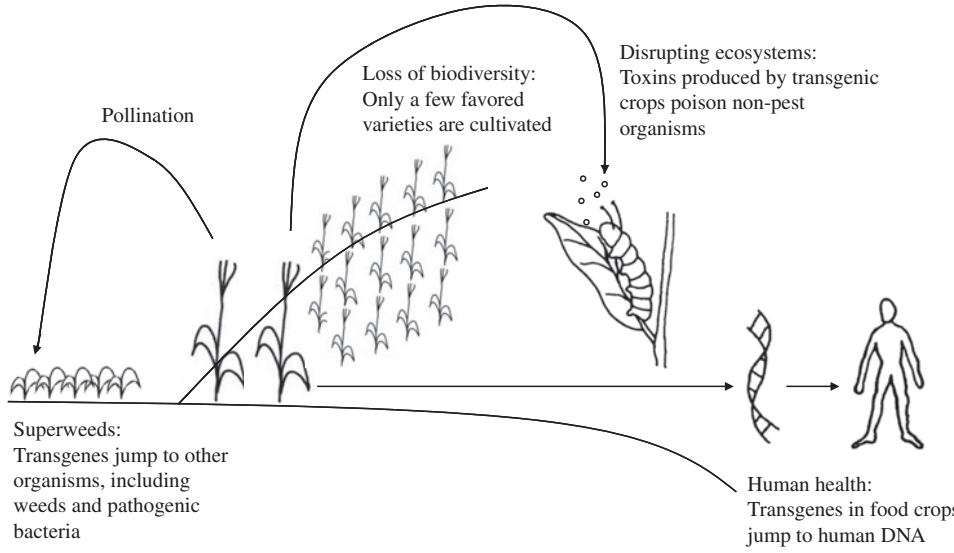

FIG. 11.1 Potential environmental impacts of plant science.

resources to appreciate pristine natural environments, there has arisen the notion of "Frankenfood," a man-made plant with toxins that poison the food supply or that is so prolific that it upsets the balance of nature.

Application of biotechnology to plant science offers several opportunities for plant improvements, including resistance to herbicides, protection against insects and other pests, hardiness against frost, and the manufacture of valuable products in plants. The latter of these possibilities, many believe, is the key to future growth in the development of biobased products. The concerns about the environmental impact of transgenic crops must be addressed early in their development if this future is to be realized. Some of the most prominent environmental concerns about transgenic crops are illustrated in Figure 11.1 and discussed in the following paragraphs.

As described in Chapter 5, the process of developing a transgenic plant requires selection of plant cells that have been successfully transformed; that is, those that have incorporated the transgene. This is commonly accomplished by inclusion of a selectable marker gene in the constructed transgene that is resistance to an herbicide or an antibiotic. Thus, application of the herbicide or antibiotic to regenerated plants kills those that do not contain the transgene, allowing the transgenic plants to be identified and selected. The prospect of these resistant genes being transferred to wild plants by pollination or to bacteria by the same kind of gene transfer between bacteria and plant cells that are frequently used to produce transgenic crops is disturbing to many people. Transfer of herbicide resistance to

weeds would be a serious threat to agriculture while transfer of antibody resistance to pathogens would threaten human health.

Transfer of herbicide resistance is a distinct possibility if transgenic crops are grown in close proximity to closely related weed species. For example, gene movements between wild mustard growing among a crop of canola and between jointed goatgrass growing among a crop of wheat have been demonstrated, raising the prospects for "superweeds." The transfer of antibiotic resistance to pathogenic bacteria is an extremely unlikely event but cannot be completely ruled out. For these reasons, alternative selection methods, such as marker genes that cause a transformed plant to fluoresce when exposed to ultraviolet light, are under development. Of course, the transfer of genes that are specifically added to make a plant resistance to herbicides or to attack by insects cannot be prevented in this manner. In this case, more sophisticated approaches to preventing the creation of superweeds are required. For example, herbicide-resistant genes could be linked to other genes that are harmless to a crop but damaging to a weed that might incorporate the transgene.

Another concern is that parts of a transgene inserted into food crops might escape the digestive tract and be inserted into human chromosomes. A specific example cited by critics of transgenic crops is the cauliflower mosaic virus (CaMV), often used as a promoter sequence in transgenic crops (recall that a promoter sequence is the on/off switch that controls where the plant gene will be expressed). Research on plasmid DNA in rice is cited as evidence that the CaMV promoter can insert itself into strands of DNA. However, the chain of events necessary for this to occur in human DNA is unlikely and has never been observed. CaMV infects several common crop plants, including cauliflower, broccoli, cabbage, bok choy, and canola, which have been consumed by animals and humans for centuries with no documented negative effects on health.

One well-publicized concern is that transgenic crops might threaten other organisms in an ecosystem by introducing toxic substances. Researchers have documented in laboratory trials that pollen from Bt corn, one of the first commercial transgenic crops, is toxic to monarch butterfly larvae. Bt corn was genetically engineered to contain a substance toxic to natural predators of the corn plant, so the fact that Bt corn pollen was toxic to insects was not particularly surprising. However, this demonstration raised the possibility that pollen drifting from a cornfield to milkweed growing in adjacent fields would poison monarch butterfly larvae that feed on milkweed plants, their principle source of nourishment. Follow-up studies indicate that pollen drift is unlikely to produce toxic levels of Bt corn pollen in adjacent fields. The original laboratory work, though, does demonstrate the delicate interplay between introduced plants and their environment.

Another argument cautions that transgenic crops will ultimately reduce biodiversity as they replace traditional crops. Inevitably, this will be true since the history of agriculture even before transgenic crops might best be described as the

adoption of a few superior varieties that replace a wider selection of traditional crops. The solution to loss of biodiversity is not to limit choices in agriculture but rather to establish collections of rare and obsolete varieties to serve as gene banks.

In developing transgenic crops, risk assessment should evaluate the following questions regarding their release to the environment: Does the introduction of a transgenic plant with resistance to a particular pest or disease exacerbate the emergence of new pests or diseases that are worse than the original? If a transgenic trait is transferred to a wild species, does their geographical expansion represent a threat to biological diversity? Would adoption of stress-tolerant plants lead to significant destruction of natural ecosystems?

11.3 Production

Agriculture can have either positive or negative impacts on the environment depending upon how it is practiced. Early cultivation of cotton and tobacco in the southern United States was notorious for quickly depleting soil fertility, requiring frequent opening of new lands for production of these crops. As illustrated in Figure 11.2, unsustainable agricultural practices result in loss of soil fertility, soil erosion, water pollution, air pollution, reduced biodiversity, and net positive emission of greenhouse gases from the soil to the atmosphere. Careful application of conservation principles can avoid or even reverse these impacts of agriculture.

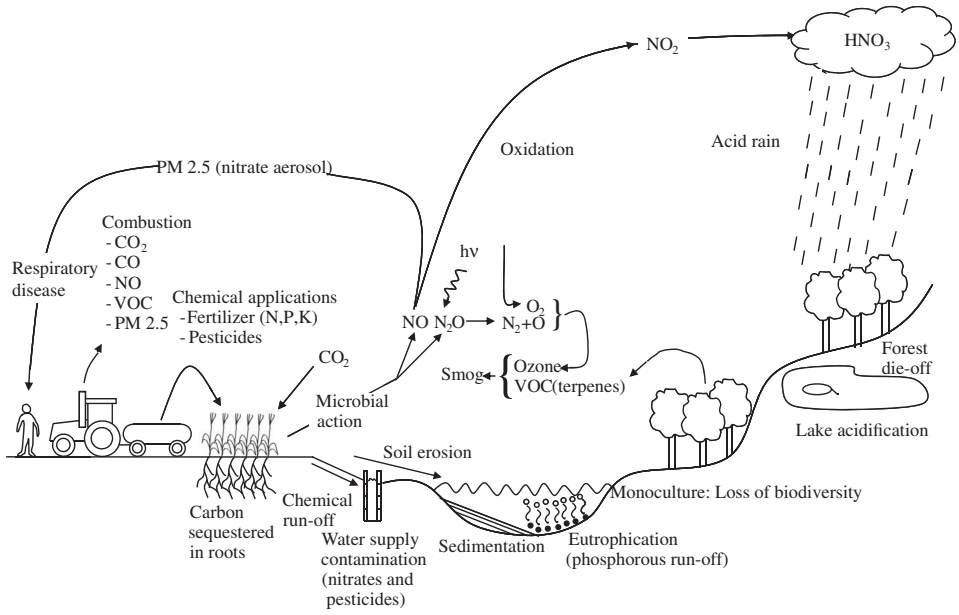

FIG. 11.2 Potential environmental impacts of crop production.

11.3.1 Soil Fertility

Soil fertility is primarily a function of the amounts of organic carbon (also known as humus), nitrogen (N), phosphorous (P), and potassium (K) in the soil. The amount of organic carbon in the soil increases or decreases from year to year depending on tillage practices. The amount of inorganic nutrients (N–P–K) in the soils of natural ecosystems is determined by a balance among wind and water transport processes and uptake by standing biomass.

Organic carbon affects soil fertility in several ways including increasing water retention capacity and gas permeability and improving the availability of inorganic nutrients to plant roots. Organic carbon is a natural product from the decay of plant material in oxygen-poor environments. This includes roots as well as aboveground stems and leaves that accumulate on the surface of soil as thatch or that is submerged in waterlogged soils. Plant material exposed to air will eventually oxidize to carbon dioxide, which is released to the atmosphere. Organic carbon was accumulated in many meters of depth in the tall grass prairies of the Midwestern United States in the period between the last Ice Age and the present era. This deep, black soil is the basis for the highly productive agriculture system in the United States. Ironically, the process of plowing these soils for agriculture exposed the buried carbon to oxidation, contributing substantially to the loss in fertility of these soils during the past 150 years. Modern conservation tillage practices can reduce and even reverse these losses.

Intensive agriculture disrupts the balance of inorganic nutrients in the soil: uptake of nitrogen, phosphorous, and potassium by standing biomass that is subsequently removed as crop leads to depletion of these nutrients from the soil faster than transport by wind or water can replace them. Consequently, inorganic nutrients must be periodically replaced by application of fertilizer. Cropping systems have widely varying fertilizer requirements, as indicated in Table 11.1. Corn, for example, is notable for its demand for nitrogen, requiring on the order of

Table 11.1 Environmental impacts of different kinds of crops

Cropping System	Soil Erosion Rate (Mg/ha/year)	N–P–K Application Rate (kg/ha/year)	Herbicide Application Rate (kg/ha/year)	Insecticide Application Rate (kg/ha/year)
Annual crops				
Corn	21.8	135–60–80	3.06	0.38
Soybeans	40.9	20–45–70	1.83	0.16
Perennial crops				
HEC	0.2	50–60–60	0.25	0.02
SRWC	2.0	60–15–15	0.39	0.01

Source: Hohenstein, W.G. and Wright, L.L. (1994) Biomass energy production in the United States: an overview. *Biomass and Bioenergy*, 6, 161–173.

135 kg/ha/year compared to only 50–60 kg/ha/year for herbaceous energy crops (HEC) and short rotation woody crops (SRWC). At the other extreme is soybean, requiring only 20 kg/ha/year of nitrogen as a result of this plant's ability to synthesize nitrogen compounds from atmospheric nitrogen through the action of symbiotic bacteria in its roots. Not only is fertilizer application expensive and energy intensive (especially nitrogen) but it also impacts water pollution, as subsequently described.

Some dedicated energy crops have the potential for improving soil fertility. Those that are perennial crops, once established, do not require annual tilling of the soil, which contributes to the loss of soil carbon by both oxidation and erosion. As Table 11.1 shows, these perennial crops also have relatively modest fertilizer requirements, especially compared to corn; thus, they deplete inorganic nutrients at relatively lesser rates. In general, establishment of dedicated energy crops in place of conventional row crops will improve soil fertility. However, this may not be true if the dedicated energy crops are established on fallow lands or pasture, especially in the early years of establishment.

11.3.2 Soil Erosion

Soil erosion is the transport of soil from one location to another, either by wind or by water. In the process, the losses of organic carbon and inorganic nutrients from one location are gained by other locations; thus, erosion is not inherently bad. In practice, though, the net effect of soil erosion is to rob fertility from lands under intensive agriculture, which reduces crop productivity and distributes soil and nutrients in unwanted locations, thus making them pollutants. Table 11.1 shows that cropping systems employing perennial crops have soil erosion rates that are one to two orders of magnitude less than for row crops such as corn and soybeans. In fact, during the first two years of establishment of perennial crops, erosion rates can be comparable to those for row crops, but these rates decrease dramatically after root systems develop and, in the case of woody crops, tree canopies close. Use of ground covers might further reduce erosion for dedicated energy crops.

11.3.3 Water Pollution

Water pollution arises from both water-induced soil erosion and leaching of chemicals (inorganic nutrients, herbicides, and insecticides) from soils. Transport of soil from cultivated fields into waterways is responsible for the notoriously muddy rivers and streams of the Midwestern United States. Suspended solids can dramatically change aquatic ecosystems, driving out game fish, for example, which are replaced by bottom feeders. Soils washed into reservoirs and lakes drop out of suspension to form sediments that seriously reduce the water holding capacity

of these impoundments, affecting both animal and human activities. Suspensions of soil can also facilitate transport of agricultural chemicals, which can attach to individual soil particles.

Leaching of chemicals from soils is roughly proportional to their application rates to cropland. Although comprehensive data is not available, as little as 40% of nitrogen applied to an annual crop is incorporated into plant matter, the balance being volatilized or leached from the soil. Table 11.1 indicates that leaching of inorganic nutrients, herbicides, and insecticides can be expected to be considerably worse for row crops than perennial energy crops.

Ammonia, the usual form of nitrogen in fertilizer, is oxidized to nitrates when exposed to air. Nitrates are readily leached from soils and can appear in both well water and river water at concentrations exceeding the 10-ppm human health standard set by the US Environmental Protection Agency (EPA). Human babies are susceptible to nitrate poisoning in the first few months of life when bacteria living in their digestive tracts convert nitrate to nitrite, which binds to hemoglobin and destroys its oxygen-carrying ability. Known as "blue baby" disease, a poisoned infant gradually suffocates. By the time a child reaches 6 months of age, stomach acids are sufficiently strong to kill the offending bacteria, and the disease is no longer a concern.

Phosphorous, which binds tightly to soil particles, is washed from fields as a result of soil erosion. Phosphorous represents a particular threat to aquatic ecosystems. In a process known as eutrophication, phosphorous promotes the rapid growth of algae near the surface of bodies of water. Eventually the algae die and their decomposition reduces dissolved oxygen to levels too low to support aquatic organisms, a condition known as hypoxia. The result is a general die-off in the body of water. The problem can reappear periodically since phosphorous accumulates in the sediments of lakes and streams. Rapid run-off during a storm can stir up sediment and release phosphorous in another cycle of eutrophication.

Potassium in drinking water is not regulated. The World Health Organization does not consider this chemical to have any impact on drinking water quality or on human health.

Herbicides and insecticides are, by definition, toxic chemicals used to control plant and animal pests. Their environmental and health effects at low concentrations are not well known, but they have been implicated as potential carcinogens and endocrine disrupters. They can be directly leached from the soil or transported by attachment to eroded soil particles. Most problems with pollution from pesticides arise from point source emissions such as occur from accidental spills or improper disposal of chemical containers. However, nonpoint source pollution can result from heavy rainfalls that occur immediately after application of pesticides to a field. Both herbicides and insecticides have been detected year-round in unconfined aquifers at very high concentrations (hundreds of parts per million). The lower pesticide application rates and the lower soil erosion rates associated

with perennial energy crops suggest that pesticide pollution will be considerably less than for conventional row crops.

11.3.4 Air Pollution

The contribution of crop production to air pollution is of two types: exhaust emissions from tractors and other production machinery and dust and gas arising from tilled soils. Exhaust emissions from internal combustion engines include nitrogen oxides, carbon monoxide, unburned hydrocarbons, and fine particulate. The impacts of these emissions on the environment are detailed in a subsequent section; however, the total emissions from production machinery are small and diffuse compared to those from the transportation and utility sectors of the economy.

Potentially more significant is the contribution of soil tillage to air pollution, which generates both particulate and gaseous pollutants. Particulate pollutants are classified as either primary or secondary particulate matter (PM), depending upon its origin. Primary PM is emitted to the atmosphere as particles, while secondary PM is frequently formed in the atmosphere by chemical reaction of gaseous pollutants. An example of primary PM is dust stirred up from dry soil when it is plowed. Primary PM produces relatively course particles, on the order of 10 μm in size.

A prominent instance of secondary PM is nitrate aerosols, which are formed by the oxidation of combustion-generated nitric oxide that has been emitted to the atmosphere. Secondary PM is produced as very fine particles, which, for regulatory purposes, is defined as being less than 2.5 μm in size. Such fine particle matter, designated as PM 2.5, is readily respired into the lungs but not out of them. PM 2.5 recently has been implicated in respiratory disease and is a regulated pollutant for some industries.

Wind-blown dust from agriculture can travel hundreds and even thousands of miles. Although a nuisance, this dust is mostly coarse PM, which is not thought to represent a health hazard. Careful soil management practices can mitigate nuisance dust from agriculture. However, agriculture can also produce secondary PM, which is mostly PM 2.5. Ammonia applied to soil as nitrogen fertilizer can escape as gas into the atmosphere where it reacts to form fine nitrate aerosol. Agriculture is not currently regulated for fine PM.

Several gaseous pollutants can arise from cultivation. Soil nitrogen, either from nitrogen-fixing bacteria or from synthetic fertilizers, is converted to nitric oxide (NO) and nitrous oxide (N_2O) by microbial processes in wet, anaerobic soils. Microbial processes in tilled soils also produce methane, a greenhouse gas; however, the vast majority of methane emissions come from animals and anaerobic digestion of animal wastes. Manure from livestock in the United States is estimated to emit about 3 million metric tons of methane annually and account for approximately 10% of the total US methane emissions.

Nitric oxide released to the atmosphere is further oxidized to nitrogen dioxide (NO_2), which results in two pollution problems. A strong oxidizing agent, NO_2 reacts to form nitric acid, which dissolves in water droplets to form acid rain. Environmental degradation from acid rain includes acidification of lakes, which kills aquatic organisms, and damage to forests and crops. Nitrogen dioxide is also critical to the formation of ground-level ozone (O_3) in a two-step reaction mediated by sunlight:

$$NO_2 + h\nu \rightarrow NO + O \tag{11.1}$$

$$O_2 + O \rightarrow O_3 \tag{11.2}$$

Ground-level ozone, also known as urban ozone, is a health hazard that has proved a serious concern in large cities where NO is formed by automobiles and power plants. It also reacts with volatile organic hydrocarbons emitted from automobiles to form photochemical smog, a mixture of aldehydes, acid gases, and peroxyacetal nitrate ($C_2H_3O_5N$) that forms a brown hazy smudge over many large cities. Smog is not only unsightly but also irritates the eyes and lungs.

Although nitrogen oxide emissions in large urban areas are clearly a major problem, it is not known whether nitrogen oxide emissions from agricultural lands are a substantial problem since little information is available on the subject. It is expected, though, that emissions from dedicated energy crops will be less than from row crops and more than from temperate forests.

Nitrous oxide is relatively stable to chemical reaction compared to NO, but it is a strong greenhouse gas. The background level of N_2O in the atmosphere has been increasing during historical times. Some researchers attribute this trend to intensive agriculture. Its possible role in global warming is discussed in a later paragraph.

Volatile organic compounds (VOC) are also emitted from growing plants. Consisting of mostly terpenes, these molecules can react with nitrogen oxides in a process akin to smog formation in large cities to produce a bluish haze, which gives the Smoky Mountains their name. This picturesque effect may be less appealing if anthropogenic emissions of nitrogen dioxides combine with biogenic emissions of VOCs in agricultural and pristine regions.

11.3.5 Biodiversity

Biodiversity describes an environment characterized by large numbers of different species of plants and animals. Agriculture traditionally has strived for just the opposite—a monoculture of one plant species, where other plants and animals are considered pests. Production of dedicated energy crops has some prospects for improving biodiversity in the agricultural landscape. Certainly, the meadow-like

setting of fields planted to perennial grasses and the forest-like setting of tree plantations more closely resemble natural ecosystems than do row crops.

In fact, there are advantages in encouraging a certain degree of biodiversity in dedicated feedstock supply systems. Multi-species production systems could reduce the risks associated with pests. Adding nitrogen-fixing plants could reduce fertilizer applications. Other plants might provide superior erosion control during establishment.

11.3.6 Greenhouse Gas Emissions

Greenhouse gases are gases that interact with infrared radiation emitted from the Earth in such a way as to trap this radiant energy in the Earth's atmosphere. Greenhouse gases are important in moderating the Earth's temperature, keeping it in a zone that is conducive to life. The principal greenhouse gases are water vapor, carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and chlorofluorocarbons, the latter arising solely from human activity while the others have both anthropogenic and biogenic origins. As the concentrations of these gases increase, the temperature of the Earth is expected to increase, although the sensitivity of temperature to greenhouse gas concentrations is the subject of much debate.

What is known with certainty is that carbon dioxide in the atmosphere has increased about 25% since measurements were first taken in 1959 and that average global temperature has been increasing steadily for the last 30 years. Other greenhouse gases are also increasing, although carbon dioxide is thought to be the most important determinant to global temperature modulation. There is little debate that increases in atmospheric greenhouse gases have been strongly influenced by human activity. The burning of fossil fuels for heat and power is implicated in much of the anthropogenic emissions, but agriculture has also played a role. The opening of the prairies in North America 150 years ago exposed rich deposits of soil carbon to oxidation and, more recently, the widespread burning of rain forests in South America continues to release large quantities of carbon dioxide into the atmosphere. The large stocks of cattle produced today and cultivation of rice are sources of methane and N_2O.

Less certain is the magnitude of global climate change and the urgency for making changes in human activity. The historical and geological records provide only limited information in this regard. Reliable temperature data have only been recorded in very recent times. Various methods for estimating temperature and atmospheric gas concentrations from the geological record suggest a positive correlation between these parameters, but these are subject to considerable interpretation. Increasingly sophisticated computer models are being developed to predict long-term climatic changes, but they remain crude approximations of the real world. Continued research is expected to provide increasingly reliable evidence on how human activity affects global climate.

If society decides to reduce emissions of greenhouse gases, then agriculture will have an important role to play. Agriculture to date has generally been a net emitter of greenhouse gases in the forms of combusted fuels and energy-intensive agricultural inputs such as fertilizer. Agriculture in many developing countries is sometimes a major source of greenhouse gases resulting from direct land-use change. Growth in developing country's populations and the subsequent increased demand for agricultural products has incentivized the conversion of virgin lands for crop production. A common method for the illicit conversion of rainforest and grassland to cropland is the "slash-and-burn" technique, whereby the preexisting biomass on the land is chopped down and burned. While the conversion of rainforests is of particular concern due to the rapid release of the large amounts of CO_2 sequestered in old growth forests and ecosystem destruction, even the conversion of grassland causes emissions due to soil carbon oxidation. Two countries in which rainforest destruction due to direct land-use change has been particularly pronounced are Brazil and Indonesia. Soybean production has increased greatly in Brazil's Amazonian states, as popularized by an image in a 2008 issue of *Time Magazine* showing a rainforest plot surrounded on three sides by soybean fields. Similarly, Indonesia is home to growing production of palm oil, a dietary lipid, which is grown on plantations that have encroached on the country's rainforests. Illegal logging is also blamed for much of the deforestation on the Indonesian island of Borneo.

More recently, concerns have arisen that direct land-use change in the developing world is also being driven by first-generation biofuels production in developed countries. Known as "indirect land-use change" (ILUC), proponents of this effect believe that widespread production of biofuels from crops historically used as food or feed (e.g., corn, soybeans) has created shortages of these crops, causing their prices to increase substantially. Assuming that first-generation biofuel production has caused these price increases, then it is also responsible for at least some of the deforestation that results from slash-and-burn agriculture in rainforest areas.

While ILUC has been discussed since the 1990s, the concept achieved widespread recognition following the publication of a paper in the journal *Science* by Timothy Searchinger and colleagues in 2008 that calculated the lifecycle greenhouse gas emissions of US biofuels when accounting for emissions from ILUC. Specifically, the paper calculated that starch ethanol from corn and cellulosic ethanol from switchgrass emitted 93% and 50% more lifecycle greenhouse gases, respectively, than gasoline. Both biofuels had previously been calculated to have lower greenhouse gas emissions than gasoline without accounting for ILUC emissions, so the Searchinger et al. (2008) paper received immense attention from the US government, academia, and the media.

Subsequent analyses, including one coauthored by most of the original co-authors to the Searchinger paper, found its results to be very sensitive to the

assumptions it made. The original analysis was flawed for another important reason; however, it failed to quantify actual rainforest destruction in Brazil during the years in the twenty-first century when US production of ethanol from starch greatly increased. Annual deforestation in the Amazon peaked in 2004 at 2.7 million hectares before falling to 0.5 million hectares in 2012. During the same period, US ethanol production (virtually all of it from corn feedstock) increased from 12 869 million liters to 50 341 million liters. In other words, while the Searchinger analysis predicted that an increase in annual US ethanol production by 56 000 million liters would result in 2 million hectares of tropical deforestation in Brazil alone, the annual rate actually fell by the same number between 2004 and 2012. While it will still only take a few years for 2 million hectares of Amazon deforestation to occur at current rates, the strong negative correlation between US starch ethanol production and rainforest destruction over the last decade suggests that any causal link between the two is tenuous at best.

Much of the decrease in Brazil's deforestation rate has been attributed to the country's enforcement of antideforestation laws, including an expansion of its space program to include the monitoring of Amazonian rainforests via satellite. While the basic mechanism behind the theory of ILUC remains plausible, Brazil's experience with deforestation in the twenty-first century suggests that other factors (such as law enforcement) can override the influence of first-generation biofuel production in the developed world on deforestation in developing countries. Brazil's experience also demonstrates why an accurate quantification of a particular biofuel's lifecycle greenhouse gas emissions under ILUC should consider actual deforestation in the affected country. While the initial greenhouse gas emissions from ILUC attributed to US starch ethanol greatly overestimated the rate of deforestation in Brazil, this will not necessarily be the case for all first-generation biofuels when other tropical countries are considered.

While the greenhouse gas emissions associated with agriculture have been extensively quantified in recent years, negative emissions (also known as carbon sequestration) are also possible. With proper practices, agriculture can not only drastically reduce greenhouse gas emissions but also sequester carbon from the atmosphere. Methane absorbs infrared radiation about 25 times more efficiently than carbon dioxide. Despite its relatively small concentration in the atmosphere, methane is thought to be responsible for 12% of the global warming effect. Thus, one of the most obvious ways for agriculture to reduce greenhouse gas emissions is to divert manure to covered anaerobic digesters where methane can be captured and used for heat and power. Although combustion of 1 mol of methane releases 1 mol of carbon dioxide, no net emission of greenhouse gas to the atmosphere occurs since the manure was derived from plants whose origin was atmospheric carbon dioxide.

Dedicated feedstock supply systems have a unique ability to sequester carbon from the atmosphere. As the plants grow, they absorb carbon dioxide from the atmosphere and convert it into carbohydrates, oils, or proteins. If the aboveground

plant material is harvested and used for bioenergy or fuels, carbon dioxide is returned to the atmosphere with no net carbon emissions. If the aboveground plant material is harvested and processed into biomaterials such as plastics or biocomposites, the associated carbon is sequestered for the life of the material, which might be as many as 50 years.

Roots, which are underground biomass, contribute to soil humus, which could be sequestered for centuries. The contribution of roots to sequestered carbon is not trivial; some perennial plants produce almost as much belowground biomass as aboveground biomass. Plantations of SRWC might increase carbon inventories of soil by 30–40 Mg/ha over a period of 20–50 years. Maximum carbon inventories might take a century to be reached.

Char produced by thermochemical processes can be sequestered even longer. Archaeological excavations of pre-Columbian *terra preta* soils in South America suggest that the carbon content of buried char remains sequestered for 1000 years or longer. Applied to agricultural lands as soil amendment and carbon sequestration agent, this carbonaceous residue of gasification and pyrolysis is known as biochar.

11.4 Processing

11.4.1 Heat and Power

The environmental performance of biorenewable resources for the production of heat and power is generally superior to that of fossil resources. Nevertheless, both kinds of resources contain various contaminants that contribute to air pollution when burned. These contaminants include nitrogen, sulfur, chlorine, and, especially for coal and municipal solid waste, heavy metals such as arsenic, cadmium, chromium, lead, and mercury. The concentrations of nitrogen, sulfur, and chlorine for different kinds of fuels are summarized in Table 11.2.

Among the fossil fuels only coal contains significant quantities of nitrogen, sulfur, or chlorine. The relatively small amounts of these contaminants in the raw feedstocks for natural gas and petroleum-derived fuels are substantially removed during the preparation of commercial-grade fuel products (with the exception of

Table 11.2 Concentration of nitrogen, sulfur, and chlorine contaminants in various kinds of fuels

	Nitrogen (wt%)	Sulfur (wt%)	Chlorine (wt%)
Gasoline	–	0.01	–
Bituminous coal	1–2	0.4–3	0.02–0.10
Refuse derived fuel	0.6–0.8	0.3–0.5	0.5–0.6
Woody crops	0.06–0.6	0.01–0.02	0.01–0.10
Herbaceous crops	0.6–1.2	0.01–0.2	0.03–0.6

diesel fuel for stationary power applications, which may contain up to 2.0 wt% of sulfur). Coal also shows the highest concentrations of heavy metals, although diesel oil can contain substantial amounts of vanadium.

Biorenewable resources usually contain less than half the amount of nitrogen as does coal. Wood from traditional lumbering operations may have as little as 0.06% nitrogen although nitrogen-fixing trees such as black locust and heavily fertilized SRWC may contain 10 times this amount of nitrogen. Agricultural residues from heavily fertilized herbaceous crops can contain as much as 1 wt% nitrogen. Biorenewable resources may contain two orders of magnitude less sulfur as coal. On the other hand, biorenewable resources may contain an order of magnitude more chlorine than coal.

Refuse-derived fuel, obtained from municipal solid waste, is a mixture of fossil resource–derived materials, such as plastic, and biorenewable resource-derived materials, such as paper. Accordingly, the amount of nitrogen, sulfur, and chlorine in refuse-derived fuel tends to be intermediate between fossil and biorenewable fuels. Some heavy metals such as cadmium and mercury can be high if care is not taken to remove metal-bearing scrap from municipal solid waste.

The potential environmental impact of processing biorenewable resources to heat and power is illustrated in Figure 11.3. These include formation of acid rain, urban ozone, smog, and PM 2.5. PM 10 arising from ash and soot in flue gas is also a source of air pollution. Incomplete combustion is a source of both VOC (often referred to as unburned hydrocarbons when arising from combustion) and carbon monoxide (CO). Water pollution from inadequate treatment of wastewater can also be a problem.

During combustion, most fuel-bound nitrogen is oxidized to nitric oxide (NO) with smaller amounts of nitrogen dioxide (NO_2) and nitrous oxide (N_2O) also being formed. These nitrogen oxides are collectively designated as NO_x. Gasification and pyrolysis convert fuel-bound nitrogen to ammonia (NH_3) and hydrogen cyanide (HCN). Unless the producer gas is chemically scrubbed, these nitrogen compounds are subsequently oxidized to NO_x when the producer gas is burned.

Based on fuel nitrogen content, coal would appear to be the worst source of NO_x, followed by biorenewable sources, with natural gas and petroleum-based fuels producing only minor amounts of NO_x. In fact, combustion of any type of fuel in air can produce large quantities of NO_x in considerable excess to the amount expected from fuel-bound nitrogen. The reason for this is that nitrogen and oxygen in air can react at high temperatures to produce NO:

$$N_2 + O_2 \leftrightarrow 2NO \tag{11.3}$$

Good combustion practice at one time dictated the use of high temperatures and high excess air (oxygen) levels to assure complete oxidation of carbonaceous fuels. However, these conditions also favor formation of NO. In fact, high levels of NO

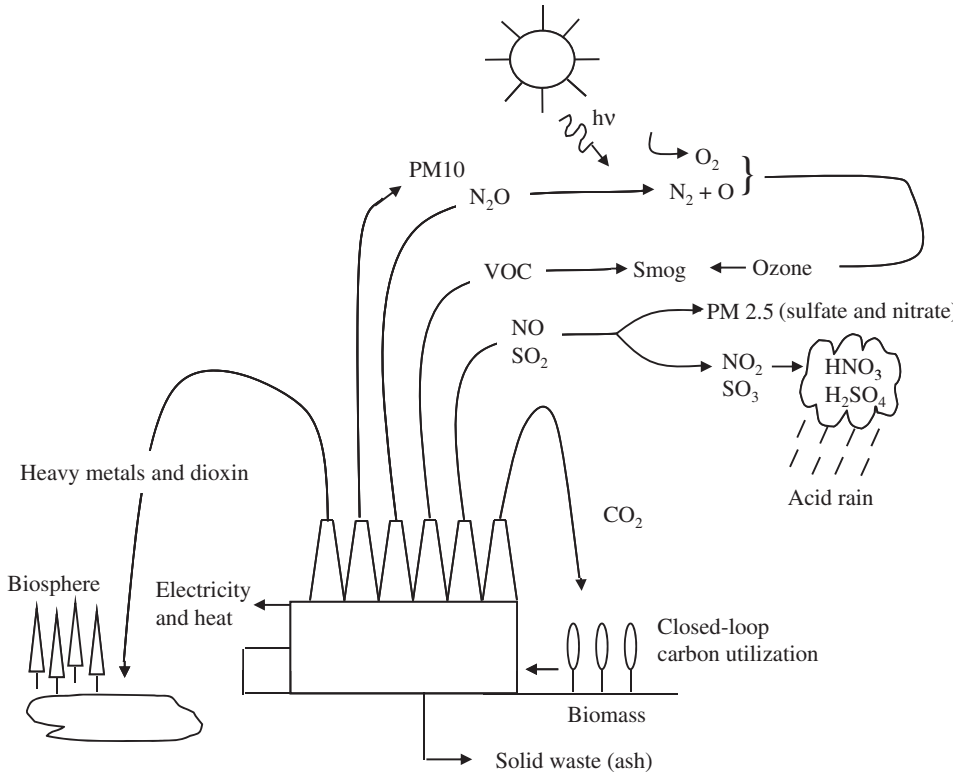

FIG. 11.3 Potential environmental impacts of processing biorenewable resources into heat and power.

in flue gas were once used as an indicator of proper boiler operation. This "thermal NO_x" was the primary source of nitrogen compounds from power plants until environmental regulation in the late twentieth century forced boiler operators to adjust operating conditions to substantially eliminate it. Today, most nitrogen compounds from power plants are "fuel NO_x" and the amount emitted from any given boiler is proportional to the nitrogen content of the fuel. However, even fuel NO_x can be reduced well below the amount expected stoichiometrically by the use of various NO_x control technologies. These include staged combustion and fuel reburning, which exploit oxygen-starved conditions to reduce NO to N_2; selective catalytic reduction (SCR), which injects amine or ammonia into flue gas to react with NO to form N_2; and selective noncatalytic reduction (SNCR), which employs a catalyst to reduce NO. The control of NO_x from liquid fuels, which contain very little fuel-bound nitrogen, is discussed under the section on fuels and chemicals.

Sulfur in fuel is oxidized to sulfur dioxide (SO_2) during combustion or released as hydrogen sulfide (H_2S) during gasification. Unless chemically scrubbed from

producer gas, H_2S will be oxidized to SO_2 when the producer gas is burned. Sulfur dioxide is further oxidized in the atmosphere to form sulfuric acid, which can form acidic water droplets or sulfate aerosols. Thus, both nitrogen oxides and sulfur dioxide contribute to the formation of acid rain and PM 2.5. Sulfur dioxide is not implicated in urban ozone or smog.

Sulfur emissions from coal-fired power plants can be controlled by reaction of metal oxide sorbents, such as CaO derived from limestone, with either SO_2 in flue gas or H_2S in producer gas. Hydrogen sulfide can also be removed by reaction with aqueous amine solutions. Biorenewable resources, which typically only contain 0.01 wt% sulfur, do not require emission controls to meet regulations on sulfur dioxide.

Fuel chlorine is converted to hydrogen chloride (HCl) during combustion, which forms hydrochloric acid upon reaction with water droplets. Hydrogen chloride, along with the oxides of nitrogen and sulfur, is known as acid gas. Unlike the other acid gases, HCl has not been implicated in formation of acid rain or PM 2.5. Because it reacts so readily with water, acid will form once flue gas drops below the dew point of the mixture of water and HCl. This usually occurs within the plant, where it can corrode equipment. Only a few fuels have sufficiently high chlorine for this to be a problem: refuse-derived fuel because of certain kinds of plastics and a few agricultural residues like wheat straw and corn stover. In these cases, scrubbing HCl from the flue gas is important to prevent equipment corrosion.

A more insidious effect arising from fuel chlorine is the formation of dioxin in combustion equipment. Dioxin refers to 210 compounds—75 dioxins and 135 furans—with similar structures and properties. Only 17 of the 210 compounds are toxic, and these differ considerably in their potency. Some of these are animal carcinogens or have been implicated in birth defects. Combustion-generated dioxin is thought to arise primarily from solid-phase reactions involving metal chlorides and fly ash carbon, which chlorinates aromatic hydrocarbons to produce dioxins. Ironically, high levels of sulfur in flue gas short-circuit the reactions that produce dioxin. For this reason, combustion of refuse-derived fuel, which contains a relatively low ratio of sulfur to chlorine, can generate high dioxin emissions, whereas combustion of coal, which typically has high sulfur-to-chlorine ratios, has not been implicated in dioxin emissions. Examination of Table 11.2 suggests that many herbaceous crops would also generate dioxin unless cofired with coal. The oxygen-starved conditions of gasification do not produce dioxins.

Incomplete combustion generates VOC and carbon monoxide (CO). Efforts to reduce NO_x emissions based on staged combustion exacerbate the emission of VOC and CO since they form under fuel-rich conditions. Any fuel, whether derived from fossil resources or biorenewable resources, can emit VOC and CO upon combustion. As previously noted, VOC plays a role in smog formation while CO contributes to cardiovascular disease. Combustion control, including

adjustment of flame position within the boiler and addition of secondary air to complete combustion, usually can achieve satisfactory levels of these products of incomplete combustion.

Heavy metals released from fuels upon combustion typically form oxides or chlorides that exist as particulate, although elemental mercury also has been detected as vapor in flue gas. The particulate is apportioned between bottom ash, which collects below the grate of certain kinds of boilers, and fly ash, most of which is captured by particulate-control devices, although some escapes into the atmosphere with the flue gas. Coal contains on the order of one-tenth of a part per million of various heavy metals while biomass crops grown on uncontaminated soil contain virtually none. Although heavy metals are present in only trace quantities, they are highly toxic and some, like mercury, are "bioaccumulators"; that is, they are taken up by plant or animal tissue and can move through the food chain where they accumulate to toxic concentrations in higher life forms. Proposals to regulate heavy metal emissions increase the attractiveness of biomass in the production of power.

When burned, solid fuels and heavy fuel oils, whether derived from fossil resources or biorenewable resources, emit primary PM in the form of ash and soot. Uncontrolled emission of these particles into the atmosphere was the most visible manifestation of air pollution before the introduction of particulate control devices. Cyclones, electrostatic precipitators, and baghouses are effective in reducing primary PM. Early regulation focused on PM finer than 10-μm size (PM 10), the most difficult fraction of primary PM to capture within the plant. More recent regulation focuses on PM 2.5, which is chiefly secondary particulate formed outside the plant, since it is considered the more serious health risk.

Properly managed heat and power production results in very little water pollution regardless of the fuel source. Wastewater is generated if fuel is cleaned before it is burned or if spray towers are used to scrub out dust, tar, or other pollutants from producer gas or flue gas. This wastewater can be a significant source of pollution if not properly handled. Indeed, many of today's federal Superfund cleanup sites are the legacy of widespread coal gasification at the turn of the century to produce "town gas" for lighting and heating. Tar in the producer gas from these early gasifiers was removed by scrubbing the gas stream with water, which was disposed of in holding ponds where the tar contaminated the soil. However, modern wastewater treatment technology is able to produce an effluent that does not contaminate the environment.

Production of heat and power is a significant contributor to greenhouse gas accumulation in the atmosphere, including nitrous oxide (N_2O), methane (CH_4), and carbon dioxide (CO_2). Although water, produced by the combustion of hydrogen-bearing fuels, is also a greenhouse gas, anthropogenic activity is not thought to substantially affect the cycling of water between the Earth's surface and the atmosphere. Nitrous oxide, although a powerful absorber of infrared radiation, can be

substantially eliminated by careful combustion control. Methane is not intentionally emitted into the atmosphere, although leaks from natural gas distribution systems can be significant if not carefully managed. The most difficult greenhouse gas to manage in the production of heat and power is carbon dioxide from the burning of carbon-bearing fuels, which includes both fossil resources and biorenewable resources. However, since biorenewable resources obtain their carbon by extracting carbon dioxide from the atmosphere, essentially no net emissions of carbon dioxide result from growing and burning biorenewable resources. The accounting of net carbon dioxide emissions is somewhat complicated by the fact that agricultural production currently employs fossil fuels to power tractors and manufacture fertilizer; however, this contribution is small and is expected to diminish as biorenewable resources are increasingly used for production of transportation fuels and chemicals.

11.4.2 Chemicals and Transportation Fuels

Processing of biorenewable resources to chemicals and transportation fuels, illustrated in Figure 11.4, can be a significant source of pollution of air, water, and soil, depending on the processes involved and the management of byproducts. Because of the diversity of these processes and byproducts, it is not possible to provide a comprehensive evaluation of their environmental impacts. Instead, the wet corn milling process will be used to illustrate the kinds of pollution problems that must be addressed in the production of chemicals and fuels.

Emission of PM is a major problem in grain handling and storage operations at a corn wet milling plant. These emissions arise from mechanical energy imparted on the corn during conveyance and can be reduced by minimizing grain free fall distances and grain transport velocities within the plant and by sealing grain receiving areas and process equipment. However, generation of some dust is inevitable, which can require ventilation systems operated in conjunction with cyclones or baghouses to control fugitive dust emissions.

The corn steep operation in wet milling plants uses 1.1–2.0 kg of SO_2 per megagram of corn. The pungent odor of SO_2 in process water dictates the enclosure and venting of process equipment. Vents can be wet-scrubbed with alkaline solution to remove SO_2 from the exhaust gas.

The most objectionable emissions from corn wet milling plants are VOC released from drying processes. In particular, drying of distillers' dried grains yields VOC with a variety of odors: acetic acid and acetaldehyde produce acrid odors; butyric acid and valeric acid yield rancid odors; and aldehydes produce fruity odors. Moderating drying temperatures can reduce the resulting blue haze from these driers. Further control is achieved with ionizing wet collectors or thermal oxidation of drier vent gases at 750°C for at least 0.5 seconds.

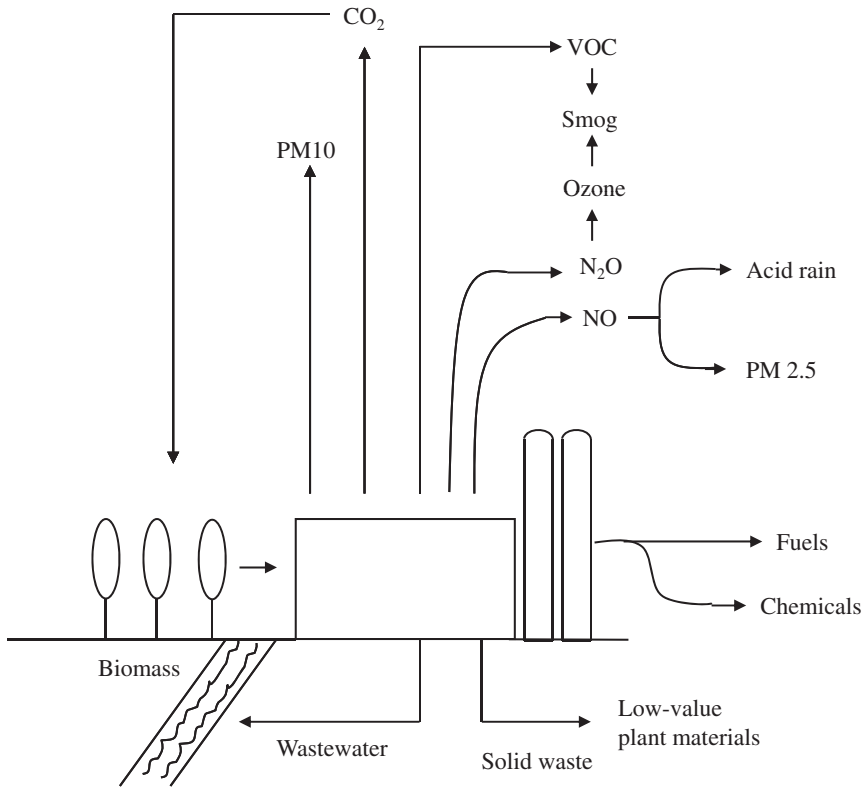

FIG. 11.4 Potential environmental impacts of processing biorenewable resources to chemicals and fuels.

If the starch product from a corn wet milling plant is used to produce ethanol as transportation fuel, two other environmental concerns are raised. The first is whether production of ethanol from corn reduces reliance on fossil fuels. Some studies have suggested that more energy is consumed in producing the grain (in the form of nitrogen fertilizer and fuel for agricultural equipment) and converting it to ethanol (especially during the energy-intensive distillation processes) than appears in the final fuel product. At the very least, it is clear that current corn-to-ethanol production and processing systems rely heavily on fossil fuels, a situation that should be addressed if ethanol is to become a major transportation fuel. Closely related to this issue is the net emission of greenhouse gases from the production of ethanol fuel from corn. Although carbon cycles from the atmosphere to the corn crop, into the ethanol product, and back to the atmosphere upon combustion as transportation fuel, the fossil fuels used in production of fertilizer, operation of tractors and combines, and distillation of ethanol contribute toward a net positive

increase in carbon dioxide to the atmosphere. To rectify this situation, future biomass-to-ethanol production should reduce the use of fossil fuels or switch to those with lower greenhouse gas emissions, such as natural gas.

Modern corn milling plants produce few water pollution or solid waste disposal problems. Wet corn milling operations produce wastewater that requires treatment. Aeration ponds are used to oxidize SO_2 to sulfate, which precipitates out into settling ponds. Corn milling produces low-value byproduct streams in the form of corn fiber from wet milling and distillers' dried grains and solubles (DDGS) from dry milling. Despite their low value, these byproducts find application as feed additives. However, if ethanol production were significantly ramped up to provide transportation fuels, these byproducts would be in excess supply and might represent a solid waste disposal problem. Landfilling of byproduct streams is already a problem in the manufacture of high-value chemicals like plant enzymes.

Cellulosic biofuel pathways avoid the issues of carbon and energy intensity by relying on a fraction of the biomass feedstock for facility power. Frequently this fraction is a low-value pathway coproduct such as separated lignin or noncondensable gases (NCG). The lifecycle GHG emissions of cellulosic biofuels are estimated to be much lower than starch ethanol as a result. Cellulosic biorefineries can still have negative impacts on the local environment, however. Like starch ethanol, cellulosic ethanol production produces a wastewater stream that must be treated prior to disposal. Excessive removal of agricultural residue feedstocks such as corn stover contributes to soil erosion from wind and water, effects that can be mitigated by leaving one-third or more of the stover produced per acre on the cropland. Finally, benzene, a carcinogen, is among the hydrocarbons produced via drop-in cellulosic biofuel pathways. Precautions must be taken during handling and distribution as a result.

11.4.3 Fibers

The early history of the pulp and paper industry demonstrates that use of biorenewable resources is not inherently environmentally benign. The notorious "paper-town smell" around pulp and paper mills came from reduced sulfur compounds, corrosive and malodorous gases arising from the use of sulfur chemicals in the pulping process. Furthermore, spent liquor discharges from paper mills turned the waters of local streams black and barren of aquatic life. In the latter half of the twentieth century, process improvements have substantially reduced these early problems, although concerns about environmental performance remain, as illustrated in Figure 11.5.

Of the two major chemical pulping processes, the sulfite process was originally preferred because of its ability to produce a lighter, easier-to-bleach pulp compared to the sulfate (kraft) process. Increasing environmental regulation gradually shifted

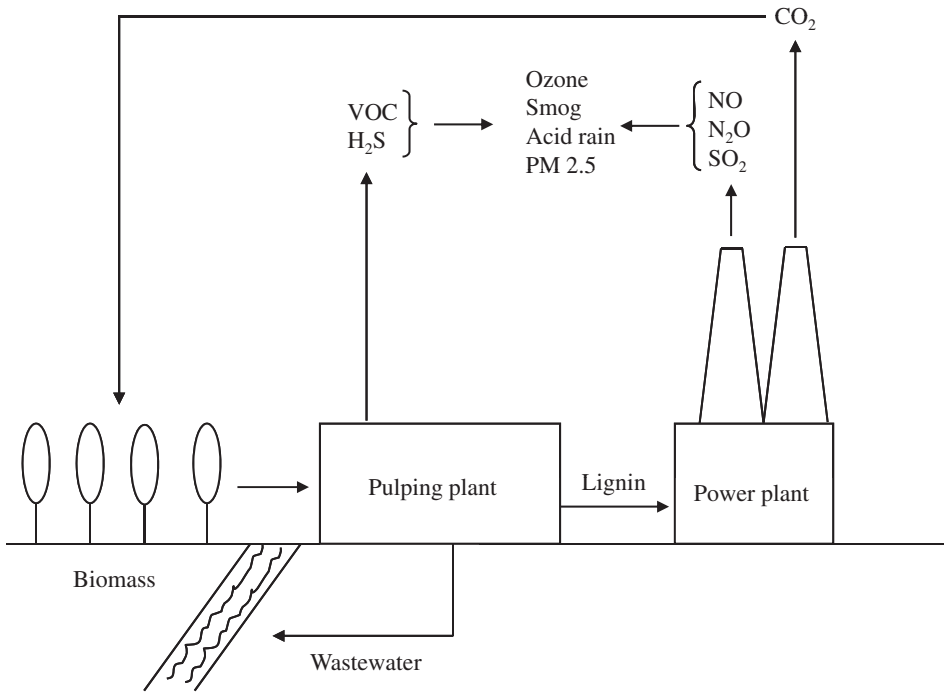

FIG. 11.5 Potential environmental impacts of processing biorenewable resources into fibers.

the industry toward the kraft process because of its ability to more economically recover chemicals from spent liquor, thus avoiding its discharge into rivers.

However, the kraft process, which requires extensive bleaching to produce white paper, introduced another environmental problem. The most economical bleaching compound is elemental chlorine (Cl_2), which reacts with organic compounds in the spent liquor to form "adsorbable" organic halogens (AOX), including dioxins and furans, some of which are very toxic to humans and animal life. Many of these organic halogens, discharged to rivers and bays, have found their way into food chains. This problem is being addressed by the adoption of elemental chlorine-free (ECF) technology, which uses chlorine dioxide, and totally chlorine-free (TCF) technology, which is based on various combinations of hydrogen peroxide, oxygen, chelating agents, and ozone treatment.

Wastewater contains cellulose fibers, polysaccharides, and various organic and inorganic compounds. Wastewaters are discharged at a rate of 20–250 cubic meters per metric ton (m^3/t) of air-dried pulp (ADP). They are high in biochemical oxygen demand (BOD), at 10–40 kg/t of ADP; total suspended solids, 10–50 kg/t of ADP; chemical oxygen demand (COD), 20–200 kg/t of ADP; and chlorinated organic

Table 11.3 Range of pollution emissions (kg/t of ADP[a]) from pulp and paper mill using the kraft process

Reduced sulfur	VOCs	Sulfur oxides	Nitrogen oxides	Particulate matter
0.3–3	15	0.5-30	1–3	75-150

Source: World Bank Group (1998) Pulp & paper mills. In: *Pollution Prevention and Abatement Handbook*. World Bank. [a]Air-dried pulp.

compounds, which may include dioxins, furans, and other adsorbable organic halides, at 0–4 kg/t of ADP.

Primary treatment is performed with a mechanical clarifier or settling pond to recover cellulose fibers, which are recycled. Chemical precipitation is used to remove certain cations. Secondary treatment is performed in aerated lagoons or anaerobic fermenters to reduce BOD by over 99%. Tertiary treatment may be performed to reduce toxicity, suspended solids, and color.

The kraft process also contributes to air emission problems. Reduced sulfur compounds, measured as total reduced sulfur, emitted to the atmosphere from the pulping process include hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. Volatile organic compounds are emitted during the concentration of black liquor in multiple-effect evaporators. Acid-precipitated lignin from the concentrated black liquor is used as boiler fuel. The remaining pollution emissions, sulfur oxides, nitrogen oxides, and PM, arise from combustion of the lignin. Table 11.3 lists the range of pollution emissions from pulp and paper mills operating on the kraft process. Emissions are reported as kilograms of pollutant per ton of ADP, which contains 10 wt% water.

11.5 Utilization

We have seen that production of biorenewable resources and their processing into biobased products can generate pollutants with adverse impacts on the natural environment. The final products themselves can also have adverse environmental impacts, either in the way they are used or in how they are disposed of at the end of their useful lives. Sometimes these impacts are not obvious until the product has been commercially introduced and its effects on the environment are monitored. Such an approach is not viable if these impacts are potentially large and negative. For this reason, lifecycle analysis, which attempts to anticipate the environmental impact of a new product from its manufacture to its final disposal, is increasingly performed before introducing a new product.

Among the most scrutinized biobased products in the United States is fuel ethanol from corn. Its environmental advantages compared to gasoline, including

its ability to reduce GHG emissions and tailpipe pollutants, have been widely touted. However, careful scrutiny reveals that environmental advantages are much harder to justify.

Fuels that contain oxygen, so called oxygenates, are reported to be more "clean-burning" than hydrocarbon fuels since complete combustion is promoted by high oxygen content of the air–fuel mixture. In principle, ethanol, which contains 35 molar% oxygen, should reduce emissions of carbon monoxide, PM, and VOC. For this reason, the US Clean Air Act Amendments of 1990 mandated the use of gasoline containing oxygenates, called reformulated gasoline, to be sold in urban areas that did not meet national targets for reducing urban ozone. The two most commonly employed oxygenates to meet this regulation were methyl tertiary butyl ether (MTBE) and ethanol. MTBE is now banned as a fuel oxygenate in some parts of the world because this toxic compound has become a serious water pollution threat.

Vehicle testing reveals that ethanol is effective in reducing carbon monoxide emissions from the carbureted engines that were in wide use when ethanol was introduced in the 1970s. However, modern automobiles employing computer-controlled, fuel-injected engines are able to achieve near-complete combustion independent of the oxygen content of the fuel, leading some critics to claim that reformulated gasoline is obsolete. The effect of ethanol on emissions of PM is not well documented.

The actual effect of ethanol on VOC emissions illustrates the importance of life-cycle analysis for new products that potentially have large environmental impacts. The marginal impact of ethanol on CO emissions from modern internal combustion engines might also be expected to be true in the case of VOC emissions, another product of incomplete combustion. In fact, there is evidence that reformulated gasoline based on ethanol exacerbates VOC emissions from automobiles as a result of increased fuel volatility: although tail pipe emissions of VOC might decrease marginally, fuel tank emissions increase significantly, from 34% of total VOC emissions from conventional gasoline to 42% of total VOC emissions from gasoline reformulated with ethanol. Evaporative emissions from fuel tanks are a direct function of fuel vapor pressure. Neat ethanol and high-level ethanol blends with gasoline have lower vapor pressures than gasoline; however, vapor pressure increases as the percentage of ethanol decreases. Reformulated gasoline, which employs only 10% ethanol, has a higher vapor pressure than conventional gasoline, thus explaining the higher VOC emissions from the ethanol blends commercially available in the United States. Blending 10% ethanol with 90% gasoline increases the fuel volatility (measured in Reid Vapor Pressure (RVP)) over that of conventional gasoline by 3.4–6.9 kPa. A possible solution to this problem is the use of ethyl tertiary butyl ether (ETBE), which does not produce this confounding effect.

Oxygenated fuels may affect NO_x emissions. Although ethanol contains no nitrogen, high oxygen levels promote thermal NO_x formation. On the other

hand, the lower flame temperature for combustion of ethanol should favor lower thermal NO_x formation. Engine testing has produced inconsistent results, but some environmentalists argue that ethanol-fueled automobiles exacerbate NO_x emissions.

Biodiesel, which is produced via transesterification of lipids, has also been found to reduce tailpipe particulate and hydrocarbon emissions relative to diesel fuel. While biodiesel does increase NO_x emissions, renewable diesel produced via hydroprocessing of lipids reduces these relative to diesel fuel as well.

Among the most attractive benefits of using ethanol fuel is reducing GHG emissions. Since the carbon in ethanol comes from plant material, the argument is that ethanol produces no net carbon dioxide emissions: an amount of carbon dioxide equivalent to that released during combustion of ethanol, which is taken up by crops, will be processed into additional ethanol. This is a potentially important role since conventional transportation fuels account for 28% of anthropogenic carbon dioxide emissions in the United States. Lifecycle analysis reveals the flaw in this argument: the current system of converting corn starch to ethanol in the United States consumes large quantities of fossil fuels that must be included in the accounting of net carbon dioxide emissions. Farm machinery is fueled by gasoline produced from petroleum. Nitrogen fertilizer is manufactured in an energy-intensive process from natural gas. Distillation of ethanol requires large quantities of energy obtained from coal or natural gas.

The range of net carbon dioxide emissions has been estimated at 15–71 kg/GJ, depending on the assumptions made for fuel source and fuel energy requirements for the conversion of corn to ethanol, how byproducts are treated, and how ILUC is accounted for. In contrast, gasoline has a net emission rate of about 76 kg/GJ. Thus, some critics claim that the superiority of corn ethanol compared to gasoline in fighting global climate change is marginal or, if a high ILUC factor is employed, nonexistent. On the other hand, ethanol produced from lignocellulosic materials has lower energy inputs during production, and all process energy comes from feedstock byproducts. Net carbon dioxide emission rates are expected to be only 8–15 kg/GJ from cellulosic biofuel production and conversion systems. Negative emission rates (i.e., net sequestration) can even be achieved by pathways such as pyrolysis when a large amount of char is produced and sequestered.

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CHAPTER
12

Economics of Biorenewable Resources

12.1 Introduction

Market acceptance of new products depends upon the complex interplay of several factors including cost, physical properties, environmental performance, public policy, and cultural prejudices. This chapter focuses on the problem of manufacturing biobased products that are cost-competitive with products already produced from petroleum or other fossil resources. Although biobased products may look attractive from other perspectives, a company will have little incentive to develop them unless the enterprise is projected to be profitable.

Accurate cost forecasting is a difficult and time-consuming activity best left to the experts. However, *cost estimating* is a valuable skill that allows an engineer to obtain "ballpark" approximations of project costs. The goal is to obtain an estimate that is within +/− 30% of the actual cost if the enterprise were pursued. Such estimates are relatively easy to develop. Additional tools such as sensitivity analysis and uncertainty analysis can be employed to identify and mitigate the distortions that this cost range has on the final result, allowing the cost estimates to be employed as an important analytical methodology.

Two kinds of costs will be considered in this chapter: the cost of producing biorenewable resource feedstocks and the cost of manufacturing biobased products from these feedstocks.

12.2 Estimating the Cost of Feedstock from Biorenewable Resources

For the purpose of cost estimating, biorenewable resources are conveniently classified as either *processing residues* from urban areas, wood mills, or agricultural processing plants; *harvesting residues* from harvesting lumber or agricultural crops; or *dedicated energy crops*. Processing residues are highly concentrated, already

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having been transported to a central processing facility, and they are often considered to be waste products. Thus, they can often be acquired at low or even negative cost with minimal transportation cost (as demand for the waste product grows, however, its cost will also increase, potentially negating this benefit). Harvesting residues are also underutilized and represent additional income for producers if they are collected and sold as a biorenewable resource. These residues are more expensive than processing residues because they must be collected from fields and transported to a central processing facility. However, development of machinery that simultaneously collects agricultural residues while harvesting the primary crop could reduce costs. Dedicated energy crops are biorenewable resources grown specifically as feedstock for the production of biobased products. Unlike agricultural residues, dedicated energy crops must bear all the expenses of cultivation and harvest; thus, they are the most expensive of the biorenewable resources. On the other hand, both kinds of residues are limited in extent to existing areas of primary crop cultivation, while the cultivation of dedicated energy crops could be expanded significantly, as described in Chapter 4.

The cost of a biorenewable resource is related to the demand for the resource by a supply curve. Figure 12.1 is a generalized representation of a supply curve for the three kinds of biorenewable resources. The least expensive is processing residues, the price of which begins to rise sharply as the supply limit is approached. Note that the supply is relatively smaller than the other kinds of biorenewable resources. Because of additional collecting and harvesting expenses, the cost of harvesting residues is significantly higher than for processing residues. The supply, however, is substantially greater. Finally, the costs of dedicated energy crops are higher than the other kinds of biorenewable resources but climbs more gradually as the demand increases. The increasing price reflects the use of less productive land to supply the

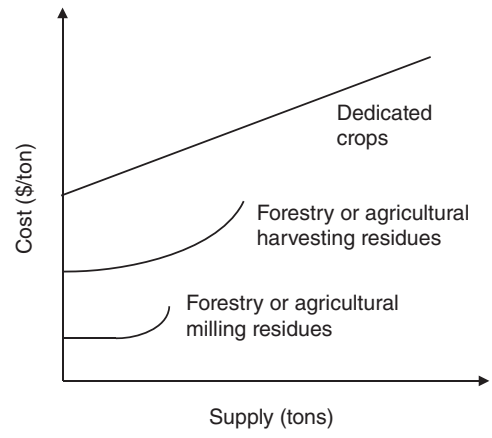

FIG. 12.1 Example of supply curves for different kinds of biorenewable resources.

Table 12.1 Availability and cost of potential US feedstocks

Feedstock	Production (10^6 Mg/year)	Price (2010 $/Mg)
Corn	107	151
Potato	18	207
Sorghum	9	180
Sugar beets	32	67
Rice	11	122
Sugar cane	27	42
Agricultural Residues and Wastes		
Low cost	59	<40
Mid cost	143	<50
High cost	162	<60
Forest Residues and Wood Wastes		
Low cost	33	<20
Mid cost	79	<40
High cost	119	<80

Sources: Crop data from US Department of Agriculture (2013) *National Agricultural Statistics Service—Statistics by Subject*.; waste and residue data from US Department of Energy (2011) *U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry*, ORNL/TM-2011/224. 148–149.

additional demand. Note that the supply curve for dedicated energy crops extends much further than the other supply curves.

The cost of biorenewable resources is highly variable and dependent on local conditions of supply and demand. This is particularly true for the processing residues and wastes, and no effort will be made to develop a methodology for estimating their costs. Instead, Table 12.1 is included to provide an estimate of availability and cost of several kinds of residues and wastes along with a comparison of the cost of a few conventional row crops. The cultivation and harvesting of dedicated energy crops, on the other hand, is amenable to standardized cost estimating since information on "unit operations," such as planting, fertilizing, and harvesting, can be readily obtained from knowledgeable sources.

12.2.1 Unit Cost for Production of Annual Crops

This methodology focuses on *annual crops* such as corn or sweet sorghum, which are planted and harvested every year. The methodology can be easily adapted to estimating the cost of harvesting residues. The methodology consists of breaking down a production system into important expense categories and assigning a cost per hectare. As shown in Table 12.2, these expense categories include preharvest machinery, seed/cuttings, fertilizer, pesticides, crop insurance, interest on short-term loans, miscellaneous, harvest machinery, labor, land, and transportation. Expenses for each expense category allow for both variable costs and fixed costs. Variable costs depend on the extent of their usage. Things such as

Table 12.2 Cost of production for annual crop

Crop:				Yield (Mg/ha/year)		Date:
Production Method:				Market Price ($/Mg)		
			Expenses		Explanation	
			Variable ($/ha)	Fixed ($/ha)		
Preharvest Machinery					Plowing, disking, fertilizing, planting, cultivating, and spraying; variable expense is fuel and repair; fixed expense is capital charges	
	$/Unit	Unit/ha				
Seed/cuttings						
Fertilizer						
Nitrogen						
P_2O_5						
K_2O						
Lime						
Pesticides						
Herbicides						
Insecticides						
Crop Insurance						
Interest					Interest on preharvest fixed variable expenses	
Miscellaneous						
Harvest Machinery					Variable expense is fuel and repair; fixed expense is capital charges	
Harvest					May involve combining or mowing, raking, and baling or forage chopping depending on the type of crop	
Haul						
Dry						
Labor					Assumed to be hired labor, a variable expense	
Land					A fixed expense whether rented or financed	
Transportation					Set to zero when calculating "farm-gate" price of crop	
Total Fixed or Variable Expense						
Total Expense					Add variable and fixed expenses	
Unit Production Cost ($/Mg)					Divide total costs ($/ha/year) by yield (Mg/ha)	

seed/cuttings, fertilizer, and pesticides are variable costs. There are also fixed costs, which are invariant during the operation and include such things as land rental and taxes. Some cost categories have both fixed and variable costs, of which machinery expenses are the most prominent example. Variable costs of machinery include fuel for operating machinery and repair to maintain machinery. Fixed costs of machinery are primarily payment of interest and principal on loans used to purchase the machinery.

Preharvest machinery expenses include plowing, disking, planting, fertilizing, cultivating, and spraying. Harvest machinery expenses depend upon the kind of crop being harvested. Grain crops involve combining; hay crops involve a series of operations, including cutting, raking, and baling; forage crops are harvested with a forage chopper; and short-rotation woody crops involve specialized cutting and chipping machinery. Machinery expenses associated with several kinds of production operations on a hectare basis can be estimated from Table 12.3, which includes information on both variable and fixed expenses of machinery operation in the state of Iowa. These numbers do not include labor costs, which are estimated separately. More detailed information can be obtained from extension services of many land-grant universities.

The cost of seed and cuttings is calculated as the product of cost per unit of seed or cutting and units planted per hectare. The unit of seed or cutting is either the number of kernels, in the case of corn, the weight of seed, or the number of cuttings, in the case of short-rotation woody crops. The units planted per hectare for a particular crop depend upon climate and soil type. Both cost per unit and units planted per hectare can be estimated for several kinds of crops from Table 12.4. The cost of fertilizer and pesticides per hectare can be estimated from Table 12.5 for several kinds of crops. More detailed information for specific agricultural regions can be obtained from extension services of many land-grant universities.

Crop insurance protects a producer against lost income in case of catastrophic crop loss associated with damage from hail, wind, or flooding. Interest is the cost of money borrowed for purchase of seed and chemicals and other preharvest variable expenses. These are short-term loans for a period roughly equal to the time between planting and harvest of an annual crop. Financing of perennial crops requiring several growing seasons before harvest requires longer-term financing and more sophisticated cost analysis, as described in Section 12.2.2. Miscellaneous expenses may include property taxes or other expenses not accounted for in the other expense categories.

Labor rates are determined by adding up the time required to perform all preharvest and harvest operations and multiplying by the hourly wage of laborers. For many cropping systems, the total labor requirement has already been determined. Hourly wages may vary considerably depending on labor availability and the skill required for the operation.

Table 12.3 Machinery costs for crop production

	Expenses ($/ha)[a]	
	Fixed	Variable
Moldboard plow	22.23	27.17
Chisel plow	9.39	11.86
Chop stalks	12.60	14.08
Tandem disk	8.89	7.66
Offset disk	10.37	10.13
Peg tooth harrow	5.19	4.45
Sprayer/disk	8.89	8.15
Field cultivator	6.18	7.66
Bulk fertilizer spreader	4.45	4.20
NH_3 applicator	11.61	13.09
Chisel plow, NH_3 application	12.35	15.56
Grain drill	10.87	10.87
Broadcast seeder	7.16	4.69
Planter	14.82	13.34
No-till planter	16.30	15.31
No-till drill	16.30	16.06
Rotary hoe	3.95	2.96
Cultivator	4.69	5.43
Sprayer	4.94	4.94
Combine corn	50.88	28.16
Combine beans	40.51	21.98
Combine small grain	30.13	13.83
Haul grain (on farm)	0.04/bu	0.04/bu
Grain cart	14.08	8.15
Silage harvester	74.1	39.77
Haul silage	1.25/Mg	1.50/Mg
Rotary mower	15.31	11.12
Mower-conditioner	13.09	11.86
Rake	9.39	6.42
Large square baler	26.68	21.49
Round baler	26.92	21.49
Windrower	7.66	5.93
Haul round bales	2.10/Mg	3.65/Mg
Forage chopper	41.00	34.83

Source: Adapted from Duffy, M. *Estimated Costs of Crop Production in Iowa—2013*, Iowa State University Extension Publication 1712.

[a]Units are $/ha unless otherwise noted.

The cost of renting land or financing the purchase of land can account for more than half the cost of production. In the case of financed purchase of land, this expense is called a capital charge and represents annual payments of principal and interest on a long-term loan. For a loan on the principal amount P taken out at interest rate i to be paid back over a period of n years, the annual capital charge A_{CC} that would appear in this expense category is

$$A_{CC} = \frac{Pi(1+i)^n}{(1+i)^n - 1} \tag{12.1}$$

Table 12.4 Costs for seed and cuttings in crop production

	Unit	Unit Cost ($/unit)	Application (units/ha)
Seed/cutting			
Corn (following soybeans)	Mg	170	11.3
Corn (following corn)	Mg	198	10.4
Soybeans (GMO)	Mg	402	3.36
Soybeans (non-GMO)	kg	410	3.36
Alfalfa	Mg	122	9.9
Short-rotation woody biomass	cutting	0.1	7200

Sources: Data for agricultural cropping systems adapted from Duffy, M., *Estimated Costs of Crop Production in Iowa—2013*, Iowa State University Extension Publication 1712; data for forestry cropping systems adapted from Wiltsee, G. and Hughes, E. (1995) Biomass energy: cost of crops and power. *Electric Power Research Institute Final Report TR-102107*, Vol. 2, October.

Unit cost of production is calculated as the total expenses ($/ha) divided by the crop yield (Mg/ha). An important expense neglected in this analysis is federal income tax that must be paid on the profits resulting from the enterprise. However, this tax is often ignored in calculating unit cost of production since it depends on all income streams for a tax-paying individual or corporation and is complicated by various depreciation allowances, accounting methodologies, and agriculture-specific tax credits. Income tax will be accounted for in the cash-flow analysis described in Section 12.2.2 for estimating unit cost of production for perennial crops.

Table 12.6 provides a cost projection for corn grown in Iowa in 2013. This analysis assumes conventional tillage following a crop of corn in the previous

Table 12.5 Costs for chemicals in crop production

			Application (units/ha)				
	Unit	Unit Cost ($/unit)	Corn following corn	Corn following soybeans	Soybeans (GMO)	Alfalfa	SRWC[a]
Fertilizer							
Nitrogen	kg	1.28	209	147	0	0	137
Phosphate	kg	1.06	70	76	45	39	See note
Potash	kg	1.10	56	61	84	140	See note
			Unit Cost ($/ha)				
Pesticides			Corn following corn	Corn following soybeans	Soybeans (GMO)	Alfalfa	SRWC[a]
Herbicide			68.50	61.75	41.50	37.30	85.00
Insecticide			46.93	0	0	0	See note

Sources: Data for agricultural cropping systems adapted from Duffy, M. *Estimated Costs of Crop Production in Iowa—2013*, Iowa State University Extension Publication 1712; data for forestry cropping systems adapted from Wiltsee, G. and Hughes, E. (1995) Biomass energy: cost of crops and power. *Electric Power Research Institute Final Report TR-102107*, Vol. 2, October 1995.

[a]Short-rotation wood crop—nitrogen applied every third year; other fertilizers dependent on soils; herbicide is applied during establishment with occasional follow-up at $38/ha; insecticide applied as needed at $2.15/ha.

Table 12.6 Example of cost of production for corn crop

Crop: Corn following corn			Yield (Mg/ha/year):	10.4[a]	Date:	2013
Production Method:	Chisel plow, tandem disk, apply N, field cultivate, plant, cultivate, and spray		Market price ($/Mg)	$276[b]		
			Expenses			
			Variable ($/ha)		Fixed ($/ha)	
Preharvest Machinery			55.82		58.54	
	$/Unit	Unit/ha				
Seed	$3.64/1000 k	74 100	269.47			
Fertilizer						
Nitrogen	$1.28/kg	209	266.46			
Phosphate	$1.06/kg	70	73.51			
Potash	$1.10/kg	56	61.75			
Lime			23.76			
Pesticides						
Herbicides			61.75			
Insecticides			46.93			
Crop Insurance			60.52			
Interest			33.39			
Miscellaneous			22.23			
Harvest Machinery						
Harvest			28.16		51.03	
Grain cart			8.15		6.70	
Haul			16.30		16.30	
Dry			78.25		20.38	
Labor					86.23	
Land (cash rent equivalent)					−681.72	
Transportation			–		–	
Total variable or fixed expense			1119.48		932.35	
Total expense			2051.83			
Unit Production Cost ($/Mg)			198.00			

Source: Data adapted from Duffy, M., *Estimated Costs of Crop Production in Iowa—2013*, Iowa State University Extension Publication 1712.

[a]Equivalent to 165 bushels per acre.

[b]Equivalent to $7.00 per bushel.

year, which affects the amount of field preparation. Note that the largest variable expenses after seed are nitrogen ($266.46/ha) and phosphate fertilizer ($73.51/ha). However, rental of land, a fixed expense, is the most important factor determining the cost of production, representing one-third of the cost of producing corn.

12.2.2 Unit Cost for Production of Perennial Crops

Perennial crops, such as hybrid poplar and switchgrass, have planting/harvest cycles that span several years and may show dramatic differences in production expenses and revenues from one year to the next. In this case, calculating production costs is more complicated because capital investment is required early in the project while significant revenue may not be generated for 2 or 3 years, in the case of switchgrass, or as long as 7 years, in the case of dedicated woody crops. Furthermore, meaningful analysis requires an accounting of the time value of money, which recognizes that a dollar spent or earned today is worth more than the same dollar in the future as a result of inflation and investment opportunities for money in the present.

The relationship between the future value, FV, and present value, PV, of a sum of money compounded annually at an interest rate, i, for a total of n years is

$$\mathrm{FV} = \mathrm{PV}(1+i)^n \tag{12.2}$$

For example, $100 invested today at 5% for 2 years will return:

$$\mathrm{FV} = \$100 \times (1+0.05)^2 = \$110 \tag{12.3}$$

Similarly, inflation at 5% per annum makes $100 worth of merchandise today cost $110 in 2 years.

Discounting is the opposite of compounding: the present value of a sum of money to be spent or received in the future is reduced according to

$$\mathrm{PV} = \frac{\mathrm{FV}}{(1+i)^n} \tag{12.4}$$

where i is now referred to as the discount rate. Thus, if the discount rate is 5% per annum, $100 to be spent 2 years hence has a present value of only

$$\mathrm{PV} = \frac{\$100}{(1+0.05)^2} = \$91 \tag{12.5}$$

Since the present value of money to be spent in the future declines with increasing interest rate and number of years into the future, the importance of accounting for the time at which money is spent or received is evident.

Cash-flow analysis is a method for accounting for the time value of money. The procedure is quite simple. For each year, all inflows of cash are subtracted from all outflows of cash to obtain an annual cash flow. In the case of crop production, inflows and outflows are conveniently expressed on a per hectare basis.

The production cost procedure developed for annual crops has been modified in Table 12.7 to allow an accounting of production costs of perennial crops over several years using the cash-flow method. Note that the table still includes the major expense categories previously considered, but columns have been added for fixed and variable expenses for every year of the enterprise (assumed to be five in Table 12.7 but possibly even longer for some short-rotation woody crops). Furthermore, additional rows are included for calculating cash flow, discounted cash flow, and net present value (NPV).

Inflows consist of annual revenues A_R from the sale of products or coproducts. These revenues are calculated from market price and yield of the crop:

$$A_R\ (\$/\text{ha}) = \text{Market price}\ (\$/\text{Mg}) \times \text{Yield}\ (\text{Mg/ha}) \tag{12.6}$$

Prices vary considerably from one year to the next, and yields are strongly dependent on soil type, geographic location, and weather, so care should be taken in assigning values for the purpose of cost estimating.

Outflows are operating expenses A_{OE}, owner's capital invested in the purchase of equipment or property A_{CI}, and federal income tax A_{IT}. These expenses are subtracted from revenues to yield net cash flow A_{CF}:

$$A_{CF} = A_R - (A_{OE} + A_{CI} + A_{IT}) \tag{12.7}$$

Note that capital invested is money provided by owners of the enterprise, whereas capital charges, an expense category accounted for under operating expenses, are the annual interest and principal payments the owners make toward retiring a loan on the purchase of land and equipment.

Federal income taxes are assessed as a certain percentage of the difference between revenues A_R and certain allowable expenses and deductions. Allowable expenses include all the previously detailed operating expenses except for repayment of principal on loans, A_P.

Allowable deductions are depreciation valuations on capital equipment. Depreciation is an important tax incentive based on the idea that equipment purchased for an enterprise "wears out" over time. Depreciation allows investors to exclude from taxation the loss in value of their original capital investment. Although different rules for calculating depreciation have been devised, straight-line depreciation is commonly employed. The annual amount of depreciation A_D by this method is the difference in fixed capital cost C_{FC} and salvage value S of the equipment divided by the depreciating time period t_D, usually taken as the useful life of the

Table 12.7 Cost of production for perennial crop

Crop:				Yield (Mg/ha/year):				Date:
Production Method:				Market Price ($/Mg)				
	Expenses ($/ha)							
Year:	1		2		3		4		5		
	Fixed	Variable	Fixed	Variable	Fixed	Variable	Fixed	Variable	Fixed	Variable	
Capital Investment, A_{CI}											Owner's capital to purchase land or equipment
Preharvest Machinery											Fixed expense includes interest A_I and principle A_P on loans
Seeds/cuttings											
Fertilizer											
Pesticides											
Crop Insurance											
Interest											
Miscellaneous											
Harvest Machinery											Fixed expense includes interest A_I and principle A_P on loans
Labor											
Land											If land is financed, includes interest A_I and principle A_P on loans
Total Fixed, A_{FE} or Variable, A_{VE} Expenses											
Total Operating Expenses, A_{OE}											$= A_{FE} + A_{VE}$
Total Revenue, A_R											= Market price × yield
Federal Income Tax, A_{IT}											$= \text{Tax rate} \times (A_R - (A_{OE} - A_P) - A_D)$
Cash Flow, A_{CF}											$= A_R - (A_{OE} + A_{CI} + A_{IT})$
Discounted Cash Flow, A_{DCF}											$= A_{CF}/(1 + r)^n$
Net Present Value, NPV											$= \Sigma A_{DCF}$

equipment or as otherwise allowed by tax laws (real estate and working capital (WC), consisting of start-up inventory for a plant, cannot be depreciated):

$$A_{\mathrm{D}} = \frac{C_{\mathrm{FC}} - S}{t_{\mathrm{D}}} \tag{12.8}$$

Thus, the calculation of income taxes is made by the following relationship:

$$A_{\mathrm{IT}} = \text{tax rate} \times (A_{\mathrm{R}} - (A_{\mathrm{OE}} - A_{\mathrm{P}}) - A_{\mathrm{D}}) \tag{12.9}$$

Tax rates are strongly dependent on the income generated by the enterprise. Small agricultural enterprises may only be taxed at 10–25%, whereas large enterprises have been historically taxed at 35–40%.

Cash flows must be discounted for the year in which cash is spent or earned. Annual discounted cash flow A_{DCF} is calculated for each year n:

$$A_{\mathrm{DCF}} = \frac{A_{\mathrm{CF}}}{(1+i)^n} \tag{12.10}$$

The discount interest rate to use in this equation is one appropriate to the investment goals of the owners. It normally accounts for both the inflation rate f of money for the period of investment and a real rate of return r. This so-called nominal rate of return i is obtained as the geometric mean of the inflation rate and real rate of return:

$$1 + i = (1 + f) \times (1 + r) \tag{12.11}$$

An excellent approximation to this relationship is

$$i = f + r \tag{12.12}$$

Summing over all the annual discounted cash flows yields the NPV of the enterprise:

$$\mathrm{NPV} = \sum_{n} A_{\mathrm{DCF}} \tag{12.13}$$

Clearly, a positive NPV at the end of the investment period indicates an investment that exceeds the desired discount rate, while a negative value indicates one that does not achieve the desired rate. If the discount rate is adjusted to achieve an NPV of exactly zero, the resulting rate is called the internal rate of return (IRR). Alternatively, if the market price is adjusted to achieve an NPV of exactly zero, the

Table 12.8 Simplified example of discounted cash flow analysis for perennial crop production

Crop: Perennial Grass	Yield (Mg/ha): 12	Market Price ($/Mg):		$45		
Discount rate: 10%						
Year:		1	2	3	4	5
Capital invested	A_{CI}	($700)	$0	$0	$0	$0
Expenses	A_E	($300)	($250)	($250)	($250)	($250)
Revenue	A_R = yield × price	$0	$540	$540	$540	$540
Annual cash flow	$A_{CF} = A_R - A_{CI} - A_E$	($1000)	$290	$290	$290	$290
Discounted annual cash flow	$A_{DCF} = A_{CF}/(1 + i)^n$	($909)	$240	$218	$198	$180
Net present value	NPV = ΣA_{DCF}					($73)

resulting market price represents the production cost or minimum selling price (MSP) of the crop assuming the specified discount rate. This second approach is particularly useful in estimating the cost of feedstocks from biorenewable resources grown as perennial crops. It can also be employed to calculate the cost of producing biobased products over the life of a manufacturing facility.

A simplified example of discounted cash flow analysis for a perennial crop is presented in Table 12.8. The crop is assumed to be a perennial grass that is planted in the first year and harvested annually in the second through fifth years of the enterprise. Capital invested in the first year, for the purchase of land, is $700/ha (dollars enclosed in parentheses represent negative cash flows). The discount rate is chosen to be 10%, which represents the expected IRR of investors in the enterprise. Annual expenses, which are not detailed in this example, are assumed higher in the first year than subsequent years because of the cost of planting and chemical treatment (herbicide and fertilizer). Income taxes are ignored to simplify the analysis. Revenue, which starts in the second year, of $540/ha is based on a constant market price of $45/Mg and crop yield of 12 Mg/ha (obviously, both price and yield will vary from year to year in a real enterprise).

Annual cash flow in the first year is negative because no crop is harvested during the establishment year. Cumulative revenue in subsequent years must be high enough to not only offset the expenses of those years but pay for the annual expense and capital investment of the first year. To get a realistic appraisal of the time value of money, the discounting factor of $(1 + i)^{-n}$ is applied to the cash flow of the nth year to derive discounted cash flows for each year. Table 12.8 shows that revenue in early years is more valuable than revenue in later years, while expenses in early years are more costly than expenses in later years.

The cash flows over the 5 years are summed to yield the NPV of the enterprise after 5 years, which in this example is −$73/ha. Thus, the enterprise has not returned the investors their expected return of 10% per annum. In this simple

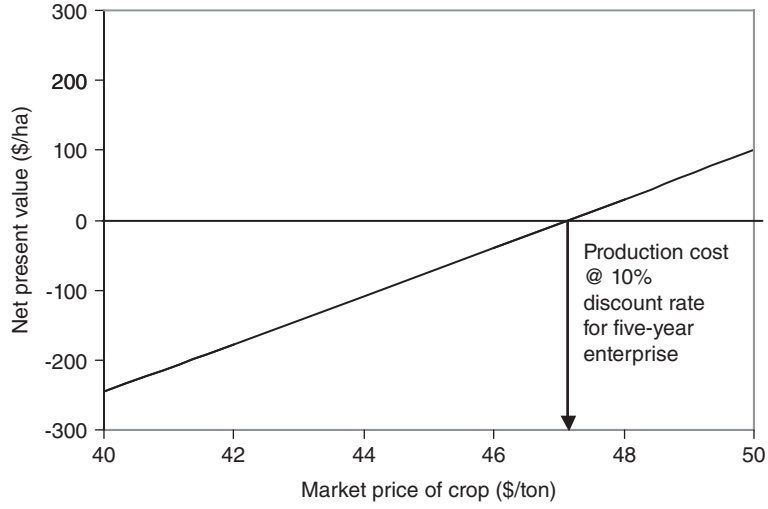

FIG. 12.2 Estimating unit cost of production for a perennial crop using cash-flow analysis (based on data in Table 12.8).

example, we can see that one additional year of harvesting would yield an NPV that was positive, unless, of course, the perennial grass had to be replanted after 5 years.

Production cost of this perennial grass over 5 years is found by plotting NPV of the enterprise after 5 years vs. assumed market price of the crop, as shown in Figure 12.2. When the market price reaches approximately $47, NPV becomes zero, representing the cost of producing the crop in the case of a 10% annual rate of return.

Table 12.9 gives estimated costs of producing several lignocellulosic feedstocks. While production and harvesting of lignocellulosic biomass has been historically limited to the pulp and paper industry, the discovery that they can be processed into high-value biofuels and bioproducts has made them attractive to both producers and manufacturers due to their abundance in nature relative to conventional row crops. Furthermore, some types of lignocellulosic feedstock can be grown on marginal land not suitable for conventional row crop production, thereby both expanding productive acreages while mitigating the food and feed crop-displacement concerns that have risen from the use of corn and soybeans as biofuel feedstocks.

Discounted cash flow analysis is an essential tool for estimating unit cost of production for perennial crops. It also is a powerful technique for estimating costs of annual crops, even for relatively constant revenues and expenses, if the time value of loans or invested capital is to be accounted for over the life of the loan or investment period. Discounted cash flow analysis is also very important in estimating costs of manufacturing biobased products from biorenewable resources.

Table 12.9 Estimated US willing to accept price for candidate lignocellulosic feedstock

Region and Species	Price ($/Mg)
Stover	92
Alfalfa	118
Switchgrass (Midwest)	133
Switchgrass (Appalachia)	100
Switchgrass (South Central)	98
Miscanthus (Midwest)	115
Miscanthus (Appalachia)	105
Wheat straw	75
Short rotation woody biomass	89
Forest residues	78

Source: Adapted from Committee on Economic and Environmental Impacts of Increasing Biofuels Production (2011). *Renewable Fuel Standard: Potential Economic and Environmental Effects of U.S. Biofuel Policy*, pp. 125. Washington, DC: The National Academies Press.

12.3 Estimating Unit Cost for Manufacturing Biobased Products

There are two important quantities to determine in economic analysis of a process: capital cost and operating cost. *Capital cost* is the amount of money to build a plant or facility and includes all equipment and labor associated with installation of the equipment. *Operating cost* represents the annual expenses to keep a plant or facility in full production. It includes costs of feedstock and fuel, labor to operate the plant, and payment of principle and interest on loans (capital charges). Operating cost is often expressed as *production cost*, which is annual operating cost divided by annual production output.

The first step in cost estimation is to design the process to be employed in the plant or facility, whether a cellulosic ethanol facility or a fast pyrolysis facility to produce renewable gasoline and diesel fuel. The design should include a flow sheet that quantifies temperatures, pressures, and balances of mass and energy through the process. Software packages such as Aspen Plus® and CHEMCAD are available for constructing and optimizing process models capable of simulating the operations of biorenewable pathways and facilities. This information is key in specifying the cost of equipment to be purchased and installed and raw materials and utilities to be consumed in the operation of the plant. After this is done, capital costs and operating costs can be estimated.

12.3.1 Capital Costs

Capital costs are broken down into four major categories: direct costs, indirect costs, project contingency, and working capital. Each of these major categories can be broken down into subcategories to yield a summary of capital costs.

Equipment Costs

Equipment (or direct) costs include the purchase price of equipment to be installed, cost of materials required for the installation and cost of the installation itself.

Total Purchased Equipment Cost The cost of equipment is usually expressed in terms of "free onboard" (f.o.b.), which is the price paid to a supplier to crate and place equipment onboard a freight carrier. The f.o.b. equipment cost requires an accounting of freight expenses. These equipment costs can be determined by calling various suppliers and obtaining informal or formal quotes. Most will supply catalogs upon request and many maintain web sites, which may or may not include price information. A good way to identify suppliers is the Thomas Register, which is available in most technical libraries and on the Internet.

Equipment cost estimation for new technologies or complex projects can be done more quickly with tabulations found in the literature [1, 2, 3, 4, 5] or in process modeling software such as Aspen Plus. These are usually presented as charts of *purchased equipment cost (f.o.b.)* vs. an appropriate sizing parameter (volume, heat transfer area, flow rate, power, etc.).

Very frequently, cost data are not readily available for the particular size of equipment or facility of interest, and a method for scaling the cost to the appropriate size is required. However, assuming that costs of equipment are linearly related to the size of the equipment will almost always produce large errors. The *principle of economies of scale* predicts that capital costs escalate proportionally slower than the size of the facility; hence, the unit cost of a product generally decreases as the facility becomes larger.

A rational basis of comparison must scale capital costs to realistic equipment size. Recognizing that capacity of a simple piece of equipment like a water tank increases with volume (i.e., as the cube of the characteristic dimension) and that the cost of the tank, for a given wall thickness, increases with the surface area of metal plate used in its construction (i.e., as the square of the characteristic dimension), it follows that the cost of the tank increases as the two-thirds power of capacity. This idea is expressed as the following simple scaling law [3]:

$$C_{p,s} = C_{p,b}\left(\frac{S_s}{S_b}\right)^n \tag{12.14}$$

where

$C_{p,s}$ = predicted cost of the specified equipment
$C_{p,b}$ = known cost of the baseline equipment
S_s = size of the specified equipment
S_b = size of the baseline equipment
n = economy of scale sizing exponent (less than unity)

Table 12.10 Unit costs and scaling exponents for various kinds of plant equipment

Device	Sizing Parameter	Unit	Unit Cost[a]	Sizing Exponent
Process furnaces	Heating rate	kW	$982	0.85
Direct-fired heaters	Heating rate	kW	$88	0.85
Shell and tube heat exchangers	Heat transfer area	m^2	$2909	0.65
Process vessel (vertical)	Volume	m^3	$7273	0.71
Process vessel (horizontal)	Volume	m^3	$7515	0.6
Pump and driver	Flow rate×pressure head	m^3 kPa/min	$424	0.52
Compressor and driver	Power	kW	$6424	0.75
Agitators (propeller)	Power	kW	$2545	0.5
Air dryers	Volumetric flow rate	m^3/min	$9212	0.56
Blowers and fans	Volumetric flow rate	m^3/min	$96	0.68
Blenders	Volumetric flow rate	m^3/min	$33 939	0.52
Boilers (100 kPa)	Mass flow rate steam	kg/h	$3758	0.5
Boilers (4000 kPa)	Mass flow rate steam	kg/h	$5212	0.5
Centrifuges	Diameter	m	$76 362	1
Conveyer belt (0.6 m width)	Length	m	$7273	0.65
Conveyer bucket (30 tph)	Length	m	$3030	0.65
Conveyer screw (0.3 m dia.)	Length	m	$4364	0.8
Crushers (pulverizer)	Mass flow rate	kg/h	$4242	0.35
Crystallizers (forced circulation)	Mass flow rate	tpd	$52 120	0.55
Dryers (rotary, direct)	Volume	m^3	$19 394	0.42
Dryers (rotary, vacuum)	Volume	m^3	$43 635	0.69
Duct work, shop-fabricated, aluminum	Length	m	$65	0.55
Duct work, shop-fabricated, galvanized	Length	m	$97	0.55
Duct work, shop-fabricated, stainless steel	Length	m	$182	0.55
Evaporator (forced circulation)	Area	m^2	$193 935	0.7
Filter (plates and press)	Area	m^2	$8242	0.58
Filter (rotary drum)	Area	m^2	$38 787	0.63
Hoppers (conical)	Volume	m^3	$70	0.68
Mills (ball)	Mass flow rate	tph	$3636	0.65
Mills (hammer)	Mass flow rate	tph	$3394	0.85
Screens (vibrating)	Area	m^2	$21 818	0.58
Storage tanks	Volume	L	$1055	0.3

Sources: Adapted from Guthrie, K.M. (1969) Data and techniques for preliminary capital cost estimating. *Chemical Engineering*, 76, 114–142. except for unit cost and sizing exponent for dryers, which is adapted from Ulrich, G.D. (1984) *A Guide to Chemical Engineering Process Design and Economics*. New York: Wiley.; all data adjusted to 2010 dollars.

[a]Special materials of construction, operation at elevated pressures, and other factors may increase these costs.

The economy of scale sizing exponent diverges from the theoretical two-thirds value depending on the kind of equipment and sometimes on the size range of the equipment. This factor is reasonably well known from industrial practice for a variety of parts and equipment; these can be used to estimate overall costs of systems made up of such parts and equipment. Table 12.10 includes unit costs for several kinds of process equipment, adjusted to 2010 dollars, along with corresponding sizing exponents for scaling the equipment to other sizes. Keep in mind that special materials of construction, such as stainless steel, or operation at elevated pressures

or other special circumstances may substantially increase equipment costs compared to the values presented in Table 12.10. In these cases, more detailed tables, such as found in Reference 1, should be consulted to obtain more accurate cost estimates.

> **Example:** A boiler is to be purchased to generate low-pressure steam (100 kPa). What is the f.o.b. cost for a boiler with 1×10^6 kg/h steam capacity? What would be the cost of a replacement pump and driver for this boiler?

From Table 12.10 is obtained a unit cost of \$3758 for a low-pressure boiler with 1 kg/h of steam flow. Linear scaling would suggest the desired steam capacity would cost:

$$\frac{\$3758}{\text{kg/h}}(1 \times 10^6 \text{ kg/h}) = \$3.8 \text{ billion}$$

Fortunately, economies of scale result in a considerably smaller escalation of price with increasing equipment size. Also from Table 12.10 is obtained a sizing exponent of 0.5. Substituting this information into Equation 12.14 yields:

$$\begin{aligned} C_p(1 \times 10^6 \text{ kg/h}) &= C_p(1 \text{ kg/h}) \left(\frac{1 \times 10^6}{1}\right)^{0.5} \\ &= \$3758 \times 1000 \\ &= \$3.8 \text{ million} \end{aligned}$$

The replacement pump must be able to provide 1×10^6 kg/h of liquid water flow pressurized to 100 kPa. Note from Table 12.10 that the sizing parameter for pumps with drivers is the product of volumetric flow rate (in cubic meters per minute) and pressure head (in kilopascal). For the specified pump, the sizing parameter is

$$\begin{aligned} \text{Volumetric flow rate} \times \text{Pressure head} &= \frac{1 \times 10^6}{1 \times 10^3} \frac{\text{kg/h}}{\text{kg/m}^3} \left(\frac{1 \text{ h}}{60 \text{ min}}\right) \times 100 \text{ kPa} \\ &= 1667 \text{ m}^3 \text{ kPa/min} \end{aligned}$$

For this pump and driver the unit cost is \$424 and the sizing exponent for this pump is 0.52; thus, Equation 12.14 yields the replacement price for the boiler pump to be

$$C_p(1667\ \text{m}^3\ \text{kPa/min}) = C_p(1\ \text{m}^3\ \text{kPa/min}) \left(\frac{1667}{1}\right)^{0.52}$$
$$= \$424 \times 47.4$$
$$= \$20\ 098$$

Scaling relationships can also be applied to overall systems but with diminishing accuracy as the system becomes more complex. For many energy and chemical process plants, a reasonable estimate for n is 0.6, which yields the so-called "six-tenth rule" [3].

The extensive cost charts found in the literature were developed from prices effective in a particular year. Inflation can greatly increase the cost of equipment over the course of a few years and must be accounted for in estimating current equipment costs. This can be done with the relationship:

$$C_{p,c} = C_{p,p} \left(\frac{I_c}{I_p}\right) \tag{12.15}$$

where

$C_{p,c}$ = inflation-adjusted cost of equipment in current year
$C_{p,p}$ = known cost of equipment in a previous year
I_c = inflation index factor for current year
I_p = inflation index factor for the previous year in which equipment cost is known

Inflation index factors are available for different categories of equipment vs. year from a variety of sources. The Marshall and Swift (M&S) equipment index can be obtained from recent issues of *Chemical Engineering Magazine* or *The Oil and Gas Journal*. Alternatively, the consumer price index prepared by the US Bureau of Labor Statistics can be used as an estimate of inflation index factors for all classes of equipment, as given in Table 12.11.

Materials of Installation and Labor of Installation Installation of equipment can require considerable materials and labor: concrete and steel for an installation pad and support structure; electric wiring and control panels for motors; and piping and valves for water, gas, and steam utilities are among some of the more common items. Counting up all these costs represents considerable effort. Fortunately, *installation factors* have been determined for costs associated with installation of industrial equipment [1, 2, 5].

Installation factors represent the sum of different categories of installation expenses. Table 12.12 presents a range of installation factor categories and their respective values as developed by Reference 5. Each value operates as a percentage

Table 12.11 Inflation index factor based on the Consumer Price Index as published by the US Bureau of Labor Statistics[a]

Year	Inflation Index Factor	Year	Inflation Index Factor
1955	1	1984	3.88
1956	1.02	1985	4.02
1957	1.05	1986	4.10
1958	1.08	1987	4.25
1959	1.09	1988	4.42
1960	1.11	1989	4.64
1961	1.12	1990	4.89
1962	1.13	1991	5.09
1963	1.14	1992	5.25
1964	1.16	1993	5.40
1965	1.18	1994	5.54
1966	1.21	1995	5.70
1967	1.25	1996	5.87
1968	1.30	1997	6.00
1969	1.37	1998	6.10
1970	1.45	1999	6.23
1971	1.51	2000	6.44
1972	1.56	2001	6.62
1973	1.66	2002	6.73
1974	1.84	2003	6.88
1975	2.01	2004	7.06
1976	2.13	2005	7.30
1977	2.27	2006	7.54
1978	2.44	2007	7.75
1979	2.71	2008	8.05
1980	3.08	2009	8.02
1981	3.40	2010	8.15
1982	3.61	2011	8.41
1983	3.73	2012	8.59

Source: US Bureau of Labor Statistics (http://www.bls.gov/cpi/home.htm, accessed September 16, 2013).
[a]Inflation factors are normalized to the year 1955.

of the piece of equipment's purchased cost; for example, the cost of the piping required to install a piece of equipment is calculated as 10% of the equipment's purchased cost. The sum of these individual factors represents the full costs associated with equipment installation:

$$\mathrm{TIC} = \mathrm{TPEC} \times \mathrm{TIF} \tag{12.16}$$

where TIC represents the total installed costs (i.e., the full cost of the purchased and installed equipment), TPEC represents the total purchased equipment costs, and TIF represents the total install factors. The sum of the individual installation factors can vary based on the type of facility considered and the expert opinion of the analyst, although a TIF of between 2.47 and 3.02 is common in the literature on biorenewable facilities.

Table 12.12 Methodology for capital cost estimation

Parameter	Assumption
TPEC	100%
Purchased equipment installation	39% of TPEC
Instrumentation and controls	26% of TPEC
Piping	10% of TPEC
Electrical systems	31% of TPEC
Buildings (including services)	29% of TPEC
Yard improvements	12% of TPEC
Service facilities	55% of TPEC
Total Installed Equipment Cost (TIEC)	TPEC × sum of installation factors (302%)
IC	TPEC × sum of IC factors (89%)
Engineering	32%
Construction	34%
Legal and contractors fees	23%
Total Installed Equipment and Indirect Costs	TEIC + TIC
Contingency	(TEIC + TIC) × 20%
FCI	(TEIC + TIC + contingency) × LF[a]
Working Capital (WC)	15% of FCI
Land Use	6% of TPEC
TPI	FCI + WC + Land

Source: Adapted from Peters, M., Timmerhaus, K., and West, R. (2002) *Plant Design and Economics for Chemical Engineers*. New York: McGraw-Hill.

[a]Location factor.

Example: Calculate the total cost of installing the low-pressure boiler of the previous example.

The purchased equipment cost of the boiler was estimated to be $3.8 million in the previous example. From Table 12.12, the TIF is 3.02. Thus, TIC is

$$\text{TIC} = \text{TPEC} \times \text{TIF} = \$3\,750\,000 \times 3.02 = \$11\,325\,000$$

Thus, the cost to acquire and install the boiler is 202% higher than the purchased cost of the boiler.

Some references categorize the individual installation factors according to specific equipment type [6]. The "hand factors" methodology employs specific installation factors for eight categories of equipment, such as heat exchangers and pumps (Table 12.13). Multiplying the purchased cost of the equipment with the appropriate hand factor yields its installed cost. The TIEC is calculated by doing this for all purchased equipment and summing across the total results.

The "module factors" methodology expands upon the hand factors methodology by employing specific installation factors for 60 different equipment categories. The module factors divide many of the hand factor categories into subcategories,

Table 12.13 Hand factors for different equipment types

Equipment Type	Factor
Fractionating columns	4
Pressure vessels	4
Heat exchangers	3.5
Fired heaters	2
Pumps	4
Compressors	2.5
Instruments	4
Miscellaneous equipment	2.5

Source: Adapted from Brown, T.R. (2000) Capital cost estimating. *Hydrocarbon Processing*, 79(10), 93–100.

providing installation factors for multiple types of heat exchangers and pumps. The TIEC calculation for the module factor methodology is completed in the same manner as described for the hand factor methodology.

Indirect Costs

Indirect costs (IC) are expenses associated with the construction of a plant or facility that cannot be characterized as equipment, materials, or labor. The three most common IC are categorized as: *engineering expenses*; *construction overhead*; and *legal and contractors' fees*. The combined cost of *legal and contractors' fees* C_{LCF} can be estimated to be 23% of TPEC for projects in the United States. *Construction overhead* cost C_O represents such things as fringe benefits on labor (heath insurance, sick leave, vacation and holiday pay, retirement benefits); so-called burden on payroll (social security taxes, unemployment insurance, workmen's compensation); salary and benefits for supervisory personnel; rental of construction machinery and purchase of small tools; and site cleanup upon completion of a project. It can be estimated to be 34% of TPEC. *Engineering expenses* C_E include salaries and benefits for design and project engineers, office expenses, and associated overhead. It can be estimated to be 32% of TPEC.

Total direct and indirect costs (TDIC) represents all direct and indirect expenses associated with purchase and installation of a piece of equipment (TPEC + IC). *TDIC* for auxiliary facilities like complete power plants or wastewater treatment plants are sometimes tabulated. More frequently TDIC is not directly tabulated and these must be determined by estimating the expenses associated with equipment installation.

Contingency

An additional cost associated with an engineering project is *contingency cost*. Contingency refers to unexpected expenses on a project (weather-related delays,

construction errors, poor estimation of costs, etc.) and is estimated to be 20% of TDIC. Note that a well-managed project would consume little of the contingency, which then becomes profit for the construction company.

The sum of TDIC and contingency is the fixed capital investment (FCI). FCI represents the full cost of the facility that can be depreciated and includes the purchased equipment costs, installation costs, IC, and contingency. Many equipment costs provided by databases such as Aspen Plus are based on prevailing costs in the US Gulf Coast region due to the large number of chemical engineering facilities located there. If the modeled facility is located elsewhere, FCI is multiplied by a location factor (LF) to reflect different prevailing costs in other regions and countries. This step is particularly important when the modeled facility is located in a region or country without an established refining industry, as much of the equipment will not be available domestically and will incur higher costs than in the US Gulf Coast as a result. Such a scenario is possible for a biorenewable facility, as access to petroleum reserves (and therefore a refining industry) is not a predictor of access to biomass feedstock. Capital cost LFs are available in the forms of the Richardson International Construction Factors Manual™ and the ENR 20-City Construction Cost Index.

Two additional capital costs frequently accounted for are WC and land. WC represents the cash and other liquid assets available to the facility to finance its day-to-day operations. It is estimated to be 15% of FCI. Land represents the cost of purchasing the land on which the facility is to be built and is estimated to be 6% of TPEC. Neither WC nor land is accounted for in FCI because neither is treated as depreciable assets, unlike the other capital costs. WC is a short-term asset and does not lose value through use (note that this is different from the loss of value occurring due to inflation). Land is also assumed to retain its full value through the lifetime of the facility. While neither cost is accounted for in FCI, they are both added to FCI to calculate the total project investment (TPI). TPI represents the full financial outlay required for the construction of a facility, and most capital cost estimates refer to TPI rather than FCI as a result.

12.3.2 Operating Costs

Once a facility is constructed, funds are required to ensure its continuous operation. Like capital costs, operating costs include direct costs and IC. In addition, there are *capital charges* that represent payments on loans secured to construct the plant. These costs are typically calculated on an annual basis, although a quarterly basis can also be used. Once the total operating cost is determined ($/year), it is divided by the *annual production output* (units/year) to determine the *annual production cost* ($/unit).

These various costs are conveniently tabulated in a *Summary of Operating Costs*, as illustrated in Table 12.14. At the top of the table is listed the *FCI* for the project,

Table 12.14 Summary of operating costs

FCI		Excludes Working Capital and Land
Working capital (WC)		15% of FCI
Land		6% of TPEC
TPI		Sum of FCI, WC, and land
Plant capacity factor (f_0)		Fraction of year that facility operates
Production output (units/year)		Annual production in kilowatts, gallons, etc. (adjusted to account for capacity factor)
	Cost ($/year)	Description
Variable cost		
Raw materials		Calculated as: $/kg × $\dot{m}$ (kg/s) × 31.5 × 10^6 s/year × f_0
By-product credits		Value enclosed in parentheses and subtracted from other costs. $/kg × $\dot{m}$ (kg/s) × 31.5 × 10^6 s/year × f_0
Operating labor		See Table 6.2 in Reference 2
Supervisory labor		10–20% of operating labor
Utilities		See Reference 6
Maintenance and repairs		2–10% of TPI
Variable Cost Subtotal		Sum all direct operating expenses
Fixed cost		
Overhead		50–70% of the sum of operating labor, supervision, and maintenance and repair
Local taxes		1–2% of TPI
Insurance		0.4–1.0% of TPI
Fixed Cost Subtotal		Sum all indirect operating expenses
Annual Capital Charges		Annual payment of interest and principal on loan for total capital $C_{TC}\, i(1+i)^n/[(1+i)^n - 1]$
Annual Operating Cost		Sum of direct costs, IC, and annual capital charge
Product Cost ($/unit production)		Annual operating cost divided by annual production output

which is the same as the FCI determined in Table 12.12. FCI represents money that could not be easily recovered once spent (such as depreciable assets).

Another important quantity is the *capacity factor* f_0 of a facility. Most plants or installed equipment do not operate 24 hours per day or 365 days per year: output may not be required continuously; the facility may close down at night; or equipment may require frequent maintenance and repair. The capacity factor is simply the fraction of time a facility operates on an annual basis. It is important in calculating the total amount of raw materials and utilities consumed and the annual production output of a facility. It does not generally affect other production costs such as labor and capital charges since these must be paid regardless of whether the facility is being operated.

Direct Costs

Variable operating costs include raw materials, by-product credits, operating labor, utilities, maintenance and repairs, and operating supplies. These costs are a function of facility capacity factor, as a change in capacity factor will result in a corresponding change to the variable costs. *Raw materials* are the inputs to the process, such as coal for a power plant or biomass to a biorefinery. Once the cost per unit mass is determined from suppliers, data from the process flow chart can be used to calculate the annual cost of each raw material:

$$\text{Raw material cost} = C_R \times \dot{m}\,(\text{kg/s}) \times 31.5 \times 10^6\,\text{s/year} \times f_0 \tag{12.17}$$

where C_R is the unit cost of raw material (\$/kg) and $\dot{m}$ is the feed rate (kg/s) of raw material into the plant. Note that the raw material cost is proportional to the capacity factor for the plant. Many plants yield by-products during the production of a desired product; for example, char from a fast pyrolysis facility or electricity from a cellulosic ethanol facility. These represent credits in the form of facility income if they can be sold; *by-product cost* is usually enclosed in parentheses and should be subtracted from other costs when annual production cost is summed. Calculation is similar to that employed for raw material cost.

Operating labor represents wages for people who operate equipment in the plant. This quantity can be estimated from tabulations of "Operator Requirements" such as is found in Table 12.15. Obviously, simple equipment or fully automated plants may have little operating labor associated with them on an annual basis (although recall that automated equipment requires the use of an additional cost factor when calculating installed equipment costs. *Supervisory labor* includes managers and clerical staff at the facility; it can be estimated as 10–20% of operating labor.

Utilities represent such process inputs as electricity, potable water, and steam. The cost per unit can be obtained from such references as the Statistical Abstracts of the United States [9] and the Energy Information Administration's Annual Energy

Table 12.15 Operator requirements for various types of process equipment

Generic Equipment Type	Operators per Unit per Shift
Air plants	1
Boilers	1
Cooling towers	1
Water demineralizers	0.5
Electric generating plants	3
Portable electric generating plants	0.5
Mechanical refrigeration units	0.5
Wastewater treatment plants	2
Water treatment plants	2
Conveyors	0.2
Crushers, mills, grinders	0.5–1
Evaporators	0.3
Vaporizers	0.05
Furnaces	0.5
Fans	0.05
Blowers and compressors	0.1–0.2
Gas–solids contacting equipment	0.1–0.3
Heat exchangers	0.1
Mixers	0.3
Reactors	0.5
Clarifiers and thickeners	0.2
Centrifugal separators and filters	0.05–0.2
Bag filters	0.2
Electrostatic precipitators	0.2
Rotary and belt filters	0.1
Plate and frame, shell and leaf filters	1
Expression equipment	0.2
Screens	0.05
Size-enlargement equipment	0.1–0.3

Source: Adapted from Ulrich, G.D. (1984) *A Guide to Chemical Engineering Process Design and Economics*. New York: Wiley.

Outlook. Annual cost for utilities can be calculated in a manner similar to that employed for raw materials and should include capacity factor.

Maintenance and repairs can be expected even for highly reliable equipment and should be included as part of the operating costs. Typically, these will be 2–10% of FCI; the low end representing well-established, relatively simple equipment and processes and the high end for unconventional or speculative processes.

Operating supplies include replaceable materials in a plant not accounted for as part of regular maintenance. They can be estimated as 10–20% of maintenance and repair costs.

Laboratory expenses represent quality control testing or other chemical and physical analyses to support the manufacturing process. These are estimated as 10–20% of operating labor.

Expenses for *patents and royalties* occur when a process is licensed from another organization. This fee is usually fixed in advance, but for estimating purposes can

be taken as 3% of the sum of all other direct expenses. In some manufacturing processes, of course, this fee may not apply.

Fixed Costs

Fixed costs include overhead, local taxes, and insurance. Fixed costs are not a function of facility capacity factor and remain the same despite changes in the factor. *Overhead* includes fringe benefits, social security taxes, unemployment insurance, and retirement funds for workers at a facility. It can be a significant fraction of total labor costs and is usually estimated as 50–70% of costs for labor, supervision, and maintenance and repair (which is mostly labor). *Local taxes* are property taxes and can be estimated to be 1–2% of FCI. *Insurance* is 0.4–1% of FCI.

Capital Charges

Typically, a loan of capital (in the form of TPI) must be secured to build and start-up a plant. We shall assume that a loan is secured for the TPI, C_{TPI}, required to build and start-up a facility. The annual interest rate of the loan is i (expressed as a decimal fraction) and the payment period of the loan is n years. To pay off the interest and principle of this loan will require the inclusion of *annual capital charges,* C_{CC}, in the operating costs equal to:

$$C_{\mathrm{CC}} = \frac{C_{\mathrm{TPI}}\, i(1+i)^n}{(1+i)^n - 1} \tag{12.18}$$

The cost of capital can be a significant fraction of the cost of operating a facility. Depending on interest rate (which is a function of both facility risk and the underlying macroeconomic environment) and the number of years of the loan, annual capital charges can run to 5–20% of the TPI and may dominate operating costs.

As an alternative to calculating capital charges, the facility can be considered as an investment by the providers of capital (shareholders), who require a reasonable rate of return on the invested capital. In this case, an *IRR* or *return on investment* (*ROI*) can be set based on those required by investors in similar industries. Most industries acquire financing from a combination of debt and equity; while the actual ratio varies, this can be estimated as an equal split.

Annual Operating Cost and Product Cost

Once direct, indirect, and capital charges are calculated, they can be summed to give the annual operating cost of a plant. The *product cost* per unit of production is simply the annual operating cost divided by the annual production output of the plant. This number can be compared to product cost for competing processes to get an idea whether the facility is worth pursuing, although it is ultimately an

incomplete metric for determining the ability of the facility to compete in the larger economy.

12.4 Estimating the Economic Feasibility of Biorenewable Pathways

While capital cost, operating cost, capital charge, and product cost calculations provide a useful reference point for comparing the economics of different facilities employing biorenewable pathways, they suffer from two notable shortcomings. First, none of them provide a means of determining facility *economic feasibility* or its profitability under one or more economic scenarios in which market conditions and commodity prices are accounted for. Second, they are all point estimates, or single data points, and as such cannot account for volatility in market prices (and thus costs), and uncertainty in projections of input costs, output prices, process yields, etc.

The first shortcoming is remedied by employing discounted cash flow rate of return (DCFROR) analysis, which accounts for capital cost, annual operating cost, annual capital charge, annual revenue, and a discount (or interest) rate to calculate one of the three dependent variables: MSP; IRR; or NPV. Each dependent variable has unique advantages and disadvantages as an economic feasibility metric relative to the others. All three, however, account for the major economic forces that directly and indirectly impact facility operations.

The DCFROR for biorenewable facilities is similar to that used to estimate the product cost of biorenewable resources presented above. Instead of seed, fertilizer, and pesticide, however, the DCFROR for biorenewable facilities considers commodities such as biomass, electricity, and/or fossil fuels as inputs. Furthermore, whereas the majority of biorenewable resource operations focus on the production of a single resource, many biorenewable facilities are capable of producing multiple high-value products. In most cases an increase of the yield of one product results in an equal decrease of the yield of a secondary product (e.g., the tradeoff between yields of bio-oil and char). The DCFROR analysis therefore must be able to differentiate between different facility products, reflecting correlations between their respective yields and, when MSP is calculated, capable of accounting for whether a product is a primary product or a byproduct.

12.4.1 Minimum Selling Price

MSP is defined as the lowest product cost capable of yielding an NPV of zero with a predetermined IRR. In addition to direct, indirect, and capital charges, therefore, MSP also accounts for an annual discount rate. Its calculation requires a DCFROR analysis that is capable of accounting for all of these factors over the

lifetime of the facility, usually 20 years. It is the simplest of the three primary economic feasibility metrics in that its calculation requires little additional data beyond that required to calculate product cost. While the discount factor can be based on a comprehensive analysis of the economic environment in which the modeled facility operates, it is most commonly set to 10% or a similar number. MSP calculations allow for biorenewable product costs to be compared with the market prices for their non-biorenewable counterparts and some insight into the economic competitiveness of the former to be derived from the comparison. For example, if a 20-year DCFROR of a biomass gasification and Fischer–Tropsch (F–T) synthesis facility calculates an MSP of $3.00/gal for its renewable diesel fuel product, then a favorable comparison with petroleum-based diesel fuel might be made when the market price for the latter is $3.50/gal. Alternatively, investors may decide that it is a poor investment when the market price for diesel fuel is lower than the MSP. MSP calculations are less suitable for biorenewable facilities with a portfolio of products (as opposed to a single product) since they treat the MSP as the dependent variable. While this does not cause significant problems for single-product facilities, its usefulness is constrained when attempting to calculate the MSP of a facility that produces equal volumes of gasoline and diesel fuel, since the MSP can only be calculated for one or the other.

12.4.2 Internal Rate of Return

IRR is defined as the annual compounded rate of return required to make the NPV of all cash flows from an investment equal to zero. It is calculated via Equation 12.13 by solving for i when NPV $= 0$. The key difference between MSP and IRR calculations is that the latter treats the IRR as the dependent variable and uses a market price in place of MSP to determine facility cash flows. For example, the income of the aforementioned biomass gasification and F–T synthesis facility is a function of the market price of diesel fuel rather than the MSP of its renewable diesel fuel product when IRR is calculated. Since the NPV is set to zero, the facility IRR is positive when the market price of the renewable diesel fuel is higher than its product cost. The advantage of the IRR calculation is that by setting the MSP as an independent variable, the market prices of multiple products can be accounted for. Rather than treat the renewable gasoline and diesel fuel products of the fast pyrolysis and hydroprocessing facility in the above example separately, an IRR calculation treats both according to their respective market prices. This permits greater flexibility when modeling pathways with multiple products, as otherwise the products will need to be treated identically for the purposes of calculating MSP.

Accounting for market prices rather than product MSPs is especially useful when modeling facilities with longer lifespans. The twenty-first century has been characterized by high volatility in energy commodity prices, which makes it unlikely that a market price used when quantifying pathway economic feasibility in 1 year will

be accurate in following years. Incorporating 20—30-year lifespans into DCFROR analysis makes it possible to account for this volatility, generating a result that is less sensitive to contemporary energy commodity prices. One option is to base the market prices used in the DCFROR analysis on historical prices. For example, a 2008 analysis using the contemporary petroleum price to quantify the economic feasibility of a biofuel pathway would have been making an optimistic assumption since petroleum prices were at historical highs in that year, causing biofuel production to look attractive. The same analysis completed the following year, when petroleum prices fell by half, would have produced a much more conservative result. Basing the market price in the model on the average petroleum price over the previous decade eliminates the sensitivity of the model result to short-term price volatility. Alternatively, several government and private research groups forecast future energy commodity prices on the basis of current and expected market conditions (the Energy Information Administration's online "Annual Energy Outlook" database is one example). While long-term price projections can be very uncertain, they do account for anticipated changes in market conditions and therefore make it less likely that a DCFROR analysis result will be made obsolete by, for example, future increased petroleum demand in China and India or increased natural gas production in the United States.

While IRR as a measure of economic feasibility addresses the shortcomings of MSP, it does suffer from two of its own. First, IRR calculations assume the continuous reinvestment of cash flows in projects with the same rate of return as the IRR. In other words, a 20% IRR result assumes that the cash flows generated by the initial investment are continuously reinvested at a 20% rate of return. This is not always possible in reality as it is unlikely that the original facility will be continuously scaled up on an annual basis using its cash flows from the previous year. IRR calculations therefore have a tendency to overestimate the project's initial rate of return, particularly when an IRR is calculated that exceeds that which can be expected for other investments. Second, IRR represents an expected return on an initial investment and is not suited for comparing possible investments with different capital costs, as the project with the higher capital cost can yield a lower IRR even if its financial return is higher in absolute terms. Based on these two issues, IRR calculations should not be used to compare mutually exclusive investments, particularly when the capital costs are not identical.

12.4.3 Net Present Value

Whereas MSP measures facility economic feasibility on a product-unit basis and IRR measures it on a percentage-return basis, NPV is reported as an absolute value. As such, it avoids several of the shortcomings of the first two and is ideal for comparative analysis of different investments, particularly those with different capital costs. Equation 12.13 is used to calculate NPV, with a predetermined

number used for i (as with MSP calculations, 10% is common) and cash flows based on the market value of the facility product(s). A positive NPV represents an investment that adds value in discounted terms, while a negative NPV represents one that reduces value. When comparing the economics of multiple biorenewable facilities, therefore, they can be ranked according to economic feasibility on the basis of their respective NPV values. Unlike MSP, NPV can account for facilities with product portfolios rather than a single product. Unlike IRR, NPV does not overestimate the return for facilities with lower capital costs. Further, it does not automatically make unrealistic assumptions regarding the annual rate of return on cash flows of facilities with high NPVs, as i can be set to a realistic value in this regard. NPV is not as useful as MSP or NPV as an individual benchmark since it does not provide a simple reference point, and many analysts prefer using the first two for reporting the economic feasibility of individual biorenewable investments for this reason. NPV should always be used when multiple mutually exclusive biorenewable investments are being compared, however.

12.4.4 Sensitivity Analysis

When economic feasibility is calculated as a single number, whether MSP, IRR, or NPV, this result is a *point estimate*. In statistics, a point estimate is a "best estimate" of an unknown population parameter. In techno-economic analysis, a point estimate is a single result value for an analysis with a relatively high uncertainty level. Point estimate results can serve as useful benchmarks but should not be relied upon alone since they are very sensitive to the assumptions used to make the calculation.

Sensitivity analysis is an analytical methodology that quantifies and presents the sensitivity of the point estimate result to the TEA parameters. Sensitivity analysis is commonly performed by identifying the parameter value assumptions (the "baseline" scenario) and then creating "pessimistic" and "optimistic" scenarios based on set percentages of the baseline parameter values. For example, if a TEA of a starch ethanol facility employs an ethanol market value of $2/gal as the assumed (or baseline) parameter value, then the pessimistic and optimistic scenarios would use parameter values of $1.4/gal (70% of the baseline value) and $2.6/gal (130% of the baseline value) for the pessimistic and optimistic scenarios, respectively. These calculations are then repeated for all of the parameter assumptions until full pessimistic, baseline, and optimistic parameter values have been developed. Point estimate results are then calculated for each parameter value under the pessimistic and optimistic scenarios (the point estimate result for the baseline scenario does not change since its parameter values do not change), allowing for the sensitivity of the point estimate result to be quantified for each change to the parameter values, both pessimistic and optimistic. Finally, the results of the sensitivity analysis are ranked by identifying the parameters to which the point estimate

result is most sensitive. The point estimates calculated for all three scenarios from changes to these parameters are presented by placing these point estimates in a chart in which the *x*-axis represents the point estimate calculation (MSP, IRR, or NPV). These charts are commonly known as "tornado plots" due to the shape that they take when the parameters are ranked vertically from greatest sensitivity to least sensitivity.

Among the parameters to which the result is most commonly reported to be highly sensitive are feedstock cost, process yield, and output market value. The choice of which values to use for these parameters therefore has a strong effect on the point estimate result, and the use of an unrealistic parameter can generate an unrealistic point estimate result. While sensitivity analysis cannot correct this, it does allow readers of the analysis to identify the unrealistic parameter values and roughly determine how replacing them individually with more realistic values affects the TEA result. Ultimately this is of limited use, however, since it does not permit for multiple values to be changed simultaneously.

12.4.5 Uncertainty Analysis

Sensitivity analysis only quantifies the sensitivity of the TEA point estimate result to isolated changes to a single parameter value. Furthermore, only a limited number of scenarios are considered. In reality these changes are not isolated, with two or more parameter values often changing simultaneously, and a very large number of possible scenarios exist. Uncertainty analysis makes it possible to determine the probability that a point estimate result will be achieved based on these different scenarios and changes to parameter values. *Monte Carlo simulation* is a methodology that utilizes repeated random sampling across hundreds or even thousands of trials to calculate numerical results, and it is commonly employed to consider techno-economic analysis under uncertainty. The ability to calculate results for a very large number of trials allows for the calculation of the probabilities that specific numerical value thresholds will be achieved by a TEA model.

The first step of Monte Carlo simulations is the completion of a sensitivity analysis. The sensitivity analysis identifies the model parameter values to which the TEA result is most sensitive, and therefore those that are worth considering further via uncertainty analysis. Monte Carlo simulations are computationally intensive by nature, a requirement that can be mitigated by only considering changes to those parameters that significantly affect the result. The second step is to develop probability distributions for those parameters identified as significant by the sensitivity analysis, for which a number of strategies exist. The simplest is to employ the distribution that is most common to the specific type of parameter. For example, many commodity price distributions over time take the form of a lognormal curve since increased demand and decreased supply in response to falling prices prevent them from ever reaching zero. A drawback of this strategy

is that the commonly used distribution is not necessarily the correct distribution for the specific parameter in question. Alternatively, when sufficient data points are available, the data can be fitted to the appropriate distribution curve. This has the advantage of ensuring that the appropriate distributions are used for each parameter, although this will not always be possible when insufficient data are available. Furthermore, cost and price parameters require historical price data for the development of distribution curves, which do not reflect recent structural shifts in the markets considered.

The third step is to identify correlations between the parameters considered by the uncertainty analysis. In many cases, particularly those involving commodities, the market values of two outputs will be closely related, and a move in one will be closely matched by a similar move in the other. For example, some biorenewable pathways produce both gasoline and diesel fuel. Since the fossil versions of both fuels are derived from petroleum, gasoline and diesel fuel prices have historically been closely correlated; it is very rare for a sharp upward movement in the price of one and a sharp downward movement in the other to occur simultaneously. Ignoring such correlations during a Monte Carlo simulation will produce an inaccurate result since it will consider scenarios that are very unlikely to occur in reality. Many simulation software packages include the ability to account for correlations in parameter values during the uncertainty analysis, and this should be done when such correlations are identified.

The final step is to run the simulation based on the probability distributions developed for the considered parameter values. As a general rule, a higher number of trials should be performed during the Monte Carlo simulation when a large number of parameters are being considered and multiple types of probability distributions have been developed. It is not uncommon for TEAs of biorenewable pathways under uncertainty to perform 10 000 or more trials. The result of the Monte Carlo simulation is commonly presented as a probability distribution for the TEA result (i.e., MSP, IRR, or NPV). This can also be presented as a continuous distribution showing the probability that specific TEA result thresholds will be met. Uncertainty analysis via Monte Carlo simulation adds an additional dimension to TEA by calculating the probability that a point estimate result will be achieved. This can have a very significant impact on the results of comparative analyses since the most attractive TEA result among multiple pathways considered may also have the lowest probability of being achieved.

12.4.6 Detailed Example of Estimating Costs for Fast Pyrolysis and Hydroprocessing

As a detailed example of cost estimating, the production of renewable gasoline and diesel fuel via fast pyrolysis and hydroprocessing is presented based on the analysis of Wright et al. [10]. A flow diagram for this biofuel production system is

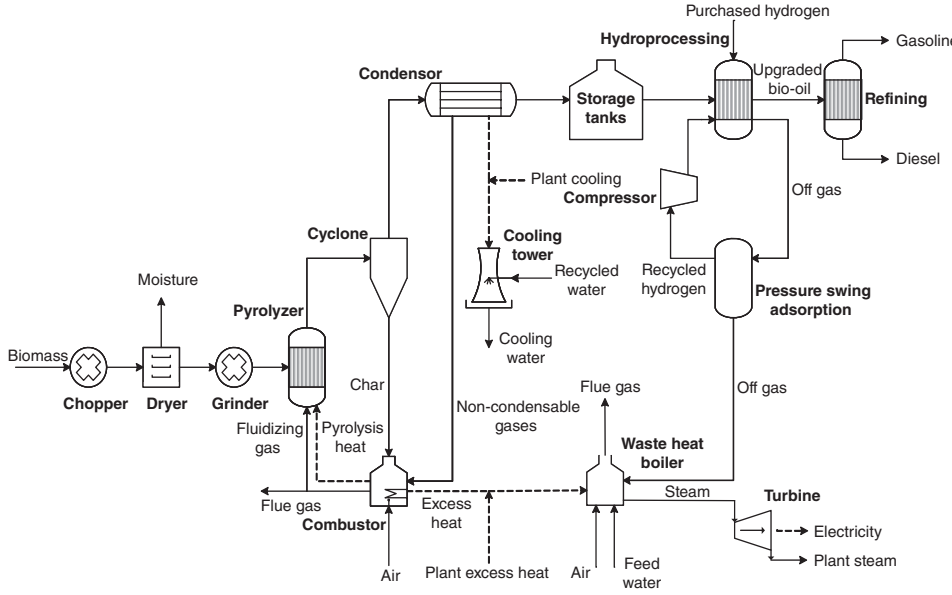

FIG. 12.3 Flow diagram for fast pyrolysis plant. Adapted from Brown, T.R., Thilakaratne, R., Hu, G., and Brown, R.C. (2013) *Fuel*, 106, 463–469.

illustrated in Figure 12.3. Two thousand metric tons per day (MTPD) of biomass feedstock is dried to 7 wt% moisture content and ground to 3-mm diameter size. The feedstock is pyrolyzed at 480°C and atmospheric pressure to yield liquid (bio-oil), solid (char), and gaseous (non-condensable gases or NCG) products. The char is removed via standard cyclones while the vapors are condensed in heat exchangers to yield bio-oil. The char and NCG are sent to a combustor providing process heat for the facility.

The bio-oil is upgraded via hydroprocessing, which consists of a low-severity hydrotreating stage followed by a high-severity hydrocracking stage. Hydrotreating occurs in a hydrogen-rich environment (about 5 wt%) at 7–10 MPa pressure and 300–400°C in the presence of a cobalt–molybdenum catalyst. The hydrotreating step removes impurities and partially deoxygenates the raw bio-oil. The hydrotreated bio-oil then undergoes hydrocracking at 10–14 MPa pressure and 400–450°C in the presence of a nickel–molybdenum catalyst. The hydrocracking step fully deoxygenates the hydrotreated bio-oil and depolymerizes its heavier constituent hydrocarbon compounds to the naphtha and diesel fuel ranges.

Plant capacity is taken to be 134 million liters per year of gasoline and diesel fuel, with equal fractions of both. The first step in estimating cost of production is to

Table 12.16 Purchased equipment costs for biomass fast pyrolysis and hydroprocessing facility example

Item	Equipment Cost C_p[a]
Pretreatment	7 046 210
Pyrolysis and oil recovery	9 744 803
Combustion	16 476 040
Hydroprocessing	16 949 520
Storage	2 027 420
Utilities	3 160 383
TPEC	55 405 410

Source: Adapted from Wright, M.M., Satrio, J.A., and Brown, R.C. (2010) Techno-economic analysis of biomass fast pyrolysis to transportation fuels. *National Renewable Energy Laboratory Technical Report NREL/TP-6A20-46586*.

[a]Adjusted to 2010 dollars.

determine the cost of equipment to be installed in the plant. Wright et al. [10] have determined equipment costs C_p for the proposed facility, which are summarized in Table 12.16 (adjusted to 2010 dollars). TPEC is $55 400 000, which is only a fraction of the cost of installing the equipment in the facility. The installation cost is calculated from factors for installation, instrumentation and controls, piping, electrical systems, buildings, yard improvements, and service facilities, which are presented in Table 12.12, as previously described. These factors and the resulting installation costs are listed in Table 12.17 for each cost category. The total cost associated with installation is $111 500 000, bringing the total installed equipment cost to $167 300 000 (the difference is due to rounding).

These numbers are the basis for preparing a summary of capital costs for the fast pyrolysis and hydroprocessing facility, which is given in Table 12.17. IC (engineering, construction, and legal and contractors' fees) are readily estimated as fractions of TPEC, as described in Table 12.12. The sum of installed equipment and IC comes to $216 500 000. Contingency is assumed to add 20% to the sum of installed equipment and IC, resulting in an FCI of $259 900 000. Working capital and land are estimated as costing $39 000 000 and $3 300 000, respectively, bringing the TPI to $302 000 000. In this case the TPI is a factor of 5.46 greater than the TPEC alone.

Sometimes the TPI is divided by the annual capacity of the plant to yield a capital cost per unit output, which in this case is $2.25 per liter of *annual biofuel capacity*. However, this number can be misleading as it suggests that capital costs are linear with plant capacity, whereas the concept of economies of scale indicates that this capital cost per unit output gets smaller as the facility gets larger. Nor should this number be confused with the production costs per unit of output, which requires a calculation of annual operating costs.

Table 12.17 Summary of capital costs for biomass fast pyrolysis and hydroprocessing facility example[a]

	Cost ($ millions)	Calculation
Equipment Costs		
TPEC	55.4	TPEC × 1
Installation	21.6	TPEC × 0.39
Instrumentation and controls	14.0	TPEC × 0.26
Piping	5.5	TPEC × 0.10
Electrical systems	17.2	TPEC × 0.31
Buildings	16.1	TPEC × 0.29
Yard improvements	6.6	TPEC × 0.12
Service facilities	30.5	TPEC × 0.55
Total installed equipment cost	167.3	TPEC × 3.02
IC		
Engineering	17.7	TPEC × 0.32
Construction	18.8	TPEC × 0.34
Legal and contractors' fees	12.7	TPEC × 0.23
Total IC	49.2	TPEC × 0.89
Contingency	43.3	(TIEC + TIC) × 0.2
FCI	259.9	TIEC + TIC + contingency
Working capital (WC)	39.0	FCI × 0.15
Land	3.3	TPEC × 0.06
TPI	302.2	FCI + WC + land

Source: Adapted from Wright, M.M., Satrio, J.A., and Brown, R.C. (2010) Techno-economic analysis of biomass fast pyrolysis to transportation fuels. *National Renewable Energy Laboratory Technical Report NREL/TP-6A20-46586*.

[a]Hydrogen production scenario.

A summary of operating costs for this fast pyrolysis and hydroprocessing facility is given in Table 12.18. Raw materials include biomass feedstock, catalysts, and process water. Utilities include electricity and solids disposal. Credits are obtained on the fraction of the char not combusted for process heat and the fuel gas produced during hydroprocessing. Other expenses were based on percentages of capital costs and operating labor as detailed in Table 12.14. Total annual operating cost is estimated at $67 280 000 per year, which represents a unit production cost of $0.502 per liter.

An abbreviated version of the facility cash flows is presented in Table 12.19. Note that it only operates at partial capacity in Year 1 due to a 6-month start-up period. Positive taxable income is not achieved until Year 5 due to depreciation and the ability to carry losses (in the form of negative taxable income) forward. The annual present value is calculated as a function of the annual cash income and the appropriate compounded discount factor for the year in question. The cash flow presented in Table 12.19 sets the MSP as the dependent variable; the discount factor (or IRR) is set to 10%. Microsoft Excel's Goal Seek function is

Table 12.18 Summary of operating costs for a biomass fast pyrolysis and hydroprocessing facility[a]

FCI	$259.9 × 10^6	WC	$39.0 × 10^6	TPI	302.0 × 10^6
Plant capacity factor		Facility capacity (10^6 l/yr)	$134 × 10^6$ liters/year		
		Cost ($10^6/yr)	Description		
Variable expenses					
Raw materials					
Feedstock		57.24	$83/metric ton		
Catalyst		1.86			
Process water		0.06			
Raw materials subtotal		59.16			
By-product credits					
Fuel gas		(10.20)	$5/MMBTU		
Char pressure		(1.69)	$22/metric ton		
By-product credits		(11.89)			
Operating labor		1.42			
Supervisory labor		0.44			
Labor subtotal		1.86			
Utilities					
Electricity		6.07	$0.054/kWh		
Solids disposal		1.87	19.8/metric ton		
Utilities subtotal		7.94			
Maintenance		5.20	2% of TPI		
Variable Subtotal		62.27	Sum all variable operating costs		
Fixed expenses					
Overhead		1.11	60% of labor subtotal		
Insurance and taxes		3.90	1.5% of TPI		
Fixed Subtotal		5.01	Sum all fixed operating costs		
Annual Capital Charges		0	100% equity financing		
Annual Operating Cost		67.28	Variable costs + fixed costs + capital charge		
Product Cost ($/L)		0.502	Operating cost divided by facility capacity		

Source: Adapted from Wright, M.M., Satrio, J.A., and Brown, R.C. (2010) Techno-economic analysis of biomass fast pyrolysis to transportation fuels. *National Renewable Energy Laboratory Technical Report NREL/TP-6A20-46586*.

[a]Hydrogen production scenario.

used to determine the MSP that results in an NPV of zero. This yields an MSP of $0.82 per liter.

IRR and NPV can be calculated with the same data by making the MSP an independent variable and using a market price in its place. Note that this will change the "Sales" numbers in Table 12.19 since these are a function of both facility output and output product value. Assuming a fuel market value of $1 per liter and setting IRR as the dependent variable calculates the IRR necessary to achieve an NPV of zero. Goal Seek is used to calculate an IRR under these conditions of 15.4%. Alternatively, setting the IRR to 10% and keeping the same fuel market value yields an NPV of $128 million.

Table 12.19 Summary of cash flows for a fast pyrolysis and hydroprocessing facility[a]

		Year									
Category	Description	1	2	3	4	5	6	7	8	...	20
Sales	Annual sales	95.2	127.0	127.0	127.0	127.0	127.0	127.0	127.0	127.0	127.0
Costs	Annual product cost	69.2	77.3	77.3	77.3	77.3	77.3	77.3	77.3	77.3	77.3
Depreciation	Straight line	74.3	53.0	37.9	27.0	22.5	22.5	22.5	0	0	0
Net revenue	Sales − costs − depreciation	(48.2)	(3.4)	11.8	22.6	27.1	27.1	27.1	49.7	49.7	49.7
Losses forward	Losses (if any) carried forward from previous year for tax purposes	0	(48.2)	(51.6)	(39.8)	(17.1)	0	0	0	0	0
Taxable income	(Net revenue − losses forward)	(48.2)	(51.6)	(39.8)	(17.1)	10.0	27.1	27.1	49.7	49.7	49.7
Income tax	0.39 × taxable income	0	0	0	0	3.9	10.6	10.6	19.4	19.4	19.4
Cash income	Sales − costs − income tax	26.1	49.7	49.7	49.7	45.8	39.1	39.1	30.3	30.3	30.3
Discount factor	10% discount rate	0.91	0.83	0.75	0.68	0.62	0.56	0.51	0.47	...	0.15
Present value	Cash income × compounded discount rate	23.8	41.1	37.3	34.0	28.4	21.9	19.9	14.2	...	4.5

Source: Adapted from Wright, M.M., Satrio, J.A., and Brown, R.C. (2010) Techno-economic analysis of biomass fast pyrolysis to transportation fuels. *National Renewable Energy Laboratory Technical Report NREL/TP-6A20-46586*.

[a]Hydrogen production scenario.

12.5 Costs of Manufacturing Various Biobased Products

12.5.1 Diesel Fuel from Gasification of Lignocellulosic Biomass [11]

The capital and operating costs for gasification and F–T synthesis with coal and natural gas are relatively well known because of significant operating experience with these systems. While lignocellulosic biomass feedstock introduces unique requirements to the pathway, much of the equipment and operating specifications are similar. The capital cost for a new plant ranges between $4.04 and $4.31 per liter of gasoline-equivalent capacity in 2010 dollars. Accordingly, a 2000 MTPD biomass gasification and F–T synthesis facility would cost between $524 million and $637 million. Assuming a cost of $83/metric ton for biomass, the MSP for diesel fuel produced via the pathway is about $1.11–$1.39 per liter in 2010 dollars.

12.5.2 Gasoline from Gasification of Lignocellulosic Biomass [12]

Lignocellulosic biomass can also be gasified to produce gasoline via methanol-to-gasoline (MTG) synthesis, which was commercialized in the 1980s to convert natural gas to gasoline. A 2000 MTPD incurs a capital cost of $210 million in 2010 dollars ($3.81/gal). The MSP for gasoline is $2.05/gal, assuming that the coproduct LPG is sold for $1.61/gal and the feedstock is available at an optimistic price of $59/metric ton.

12.5.3 Ethanol from Lignocellulosic Biomass via Enzymatic Hydrolysis and Fermentation [13]

The cost of producing ethanol from lignocellulosic biomass varies tremendously depending on the feedstock employed, facility capacity, and the choice of pretreatment and hydrolysis processes. Depending on feedstock pretreatment process, capital costs for a 2000 MTPD enzymatic hydrolysis and fermentation facility are between $380 million and $527 million in 2010 dollars. Production cost estimates vary from $0.95 to $1.27 per liter (assuming a feedstock cost of $83/metric ton). However, the volumetric heating value of ethanol is only 66% that of gasoline. This production cost is equivalent to gasoline selling from $1.43 to $1.91 per liter before tax, transportation, or profit. In contrast, refinery price for gasoline is about $0.80 per liter. Currently, the economics of fermentation is such that the commercial viability of ethanol is entirely dependent on government incentives.

12.5.4 Renewable Diesel and Jet Fuels from Lipids via Hydroprocessing [14]

Capital costs for the production of renewable diesel and jet fuel via lipids hydroprocessing are relatively low, with a 377 MLY facility incurring a cost of $225 million, or $0.60 per liter in unit capital costs. The production cost is between $1.01

and $1.33 per liter, depending on the facility capacity, the product portfolio, and whether the hydrogen is produced on-site or purchased from an external supplier. Feedstock cost is the major reason for the pathway having relatively high production costs despite lower capital costs; soybean oil feedstock contributes $0.70 per liter to the biofuel's production cost, for example. Waste fats such as those produced by animal processing facilities are a cheaper feedstock that has been used by some biofuel producers, although its total supply is limited relative to that of lipids from conventional row crops.

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CHAPTER
13

Biorenewable Policy

13.1 Introduction

The primary reason for the predominance of fossil fuels in the energy sector over the last century has been their low cost relative to biorenewables. Coal, natural gas, and petroleum have rarely been unable to compete economically against biomass, and declines in the market share of one fossil fuel have almost always been to the benefit of another. In terms of dollars per unit of energy, fossil fuels have been (and remain) among the least expensive feedstocks available to the energy sector. This has allowed them to become economically entrenched, especially within developed economies. During the twentieth century this dependence often resulted in the creation of government programs designed to encourage the exploitation of fossil fuel resources. While some biorenewable pathways historically gained traction during times of global crisis, such as biodiesel in the United States and cane ethanol in Brazil during the petroleum shortages caused by the World War II, fossil fuels quickly regained their former market share after the supply disruptions passed.

In the 1970s, one geological and two geopolitical supply shocks caused US policymakers to reconsider their country's reliance on petroleum as the primary transportation fuel feedstock. In 1956, a petroleum geologist for Shell Oil named M. King Hubbert forecasted a steady fall in the United States petroleum production beginning in the 1970s. US production did peak in 1970 at 9637 thousand barrels per day (bpd) and, with the exception of a brief increase in the 1980s, gradually fell thereafter to 5000 thousand bpd in 2008. Formerly "energy independent" in that its domestic petroleum production exceeded its petroleum imports; the UnitedStates was forced to compensate for this decline by sourcing more of its supply from foreign suppliers. In 1977, US petroleum imports surpassed domestic production for the first time of the post-war period and have continued to do so ever since.

The risks of relying on foreign petroleum to meet domestic demand became apparent to the United States in 1973 when the Organization of Petroleum Exporting Countries (OPEC) embargoed petroleum exports to the United States in

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response to the latter's support of Israel during the Yom Kippur War. The US price of imported petroleum tripled, and extensive supply shortages arose as the Nixon Administration began imposing price controls in an attempt to keep the prices down. Import prices did stabilize and even decline a bit after the embargo ended in 1974, although they remained well above their pre-embargo levels. A second shortage arose in 1979, however, following the Iranian Revolution. Iran, which had been one of the world's largest petroleum producers under the Shah, experienced a sharp decrease in production and the suspension of exports. The revolution was quickly followed by war between Iran and its neighbor Iraq, further disrupting production in the region. While other OPEC members attempted to alleviate the situation by increasing production, they were unable to prevent another doubling of US import prices, which reached a level not seen again for nearly three decades.

The twin price shocks of the 1970s spurred interest in the use of ethanol as a fuel, with 662 million liters produced in the United States in 1980. With the encouragement of the federal government, which created a fuel excise tax exemption for ethanol blends and a tariff on imported ethanol, US fuel ethanol production gradually increased to 3400 million liters in 1990 and 6200 million liters in 2000. Renewed energy security concerns following the 9/11 terrorist attacks in 2001 and the subsequent revelation that the majority of the hijackers were citizens of Saudi Arabia, one of the largest sources of US petroleum imports, caused fuel ethanol production to further increase by 1360 million liters in 2002 and 2500 million liters in 2003. In 2005, Congress passed the Energy Policy Act, which created a fuel ethanol mandate in the form of the Renewable Fuel Standard (RFS1), solidified favorable tax treatment for ethanol in the form of the Volumetric Ethanol Excise Tax Credit (VEETC), and incentivized the replacement of methyl tertiary-butyl ether (MTBE) as a fuel additive by ethanol in response to concerns over MTBE groundwater pollution. By 2008, fuel ethanol production was expanding at a rate of 10 000 million liters per year, an increase in volume that initially took 24 years to achieve. High petroleum prices and continued protectionist policies in the forms of mandates, tax credits, and tariffs made fuel ethanol production so profitable that, from 2010 to 2012, more than 50 million liters of fuel ethanol (virtually all of it from starch feedstock) was being produced in the United States annually.

Two important lessons arose from the US experience with fuel ethanol between 1980 and 2012. The period demonstrated the ability of government policy to make biorenewables economically competitive with fossil fuels over long periods of time even when fossil fuel prices are low. Fuel ethanol's share of the US gasoline market increased from 1% in 2000 to more than 10% by 2011, with the largest annual increases occurring during a period characterized by both high energy prices and significant government support. Production increased so rapidly that the first US fuel ethanol mandate, implemented in 2006, was already obsolete by 2008. Second, the US experience also demonstrated the dangers of such rapid

growth. Public concerns over the negative effects of using starch feedstocks for large-scale fuel ethanol production have resulted in the passing of legislation in many developed countries that impose restrictions on the industry's future growth and emphasize the production of other types of biofuels.

The following sections describe the major government programs that have affected biorenewable production in several countries since the 1970s and outline the types of programs that can be expected to impact biorenewable industries in the future.

13.2 Subsidies

Subsidies are one of the oldest forms of government industrial support, whether of biorenewables or otherwise. They are defined as financial assistance to producers and/or consumers to reduce the market prices of commodities. It is not uncommon for governments to subsidize commodities considered to be of great importance to their citizens; for example, Egypt's government spends billions of dollars each year on subsidies designed to keep the consumer price of diesel fuel much lower than the market price, and India heavily subsidizes imports of fertilizer for similar reasons. Subsidies can take a number of forms, although five of the most common are *income tax credits*, *direct payments*, *indirect payments*, *mandates*, and *loan guarantees*.

13.2.1 Income Tax Credits

Income tax credits are subsidies that reduce a taxpayer's income tax liability below the amount required by the statutory tax rate. The subsidy amount can be determined either by the amount of a taxpayer's expenditures (e.g., on R&D) or by the volume of its production of a particular commodity (e.g., of fuel ethanol). Income tax credits are also known as "non-refundable tax credits" in some jurisdictions. One example of a US income tax credit that was designed to promote biorenewables production is the Second Generation Biofuel Producer Tax Credit (SGBPTC), which grants qualifying producers of second-generation biofuels a credit of $1.01 against their income tax liabilities for every gallon of its cellulosic biofuel that is used as or to produce a motor vehicle fuel. In other words, a producer of 20 million gallons per year of qualifying biofuel receives a credit of $20.2 million against its income tax liability for the year, reducing its income tax liability by that amount. It is important to note that income tax credits may only be taken against the producer's income tax liability, which diminishes the subsidy's value to economically uncompetitive producers. A producer that does not achieve a profit will have an income tax liability of zero since income taxes are commonly imposed on profits, and the income tax credit will not affect a producer without any profits as a result. Income tax credits help competitive producers remain competitive but

will not make an uncompetitive producer competitive. Producers of some types of second-generation biofuels have historically struggled to compete with fossil fuels, and the SGBPTC has had limited impact as a result.

13.2.2 Direct Payments

Direct payments differ from income tax credits in that, as the name suggests, they represent a direct monetary transfer from the government to the producer. Like income tax credits, however, the amount of this transfer can be based on either the producer's expenditures or production volume. Direct payments can also be based on participation in an encouraged behavior; in Brazil, for example, qualifying parents receive direct payments from the government for ensuring that their children attend school. Direct payments are more valuable to economically uncompetitive producers than income tax credits since they are not based on their income tax liabilities and, by extension, their profitability.

One of the largest US subsidies for biorenewables historically took the form of both a tax credit and a direct payment and was officially known as a "refundable tax credit" to reflect this hybrid structure. The now-defunct VEETC, popularly known as the "Blenders' Credit", provided ethanol producers with an income tax credit of $0.45 for every gallon of anhydrous ethanol that was blended with gasoline to produce ethanol. (The exact amount of the subsidy varied over time and at one point reached $0.54/gal) The VEETC differed from the SGBPTC in that it became a direct payment as soon as the value of the income tax credit exceeded the producer's income tax liability. As an example, assume that a fuel ethanol producer has a $10 million income tax liability in a given year and 50 million gallons of anhydrous ethanol production for the same year. Assuming that all of the ethanol was blended with gasoline, then only the first 22 million gallons of production would count as an income tax credit against the producer's income tax liability. Whereas the SGBPTC would cease to apply at this point, the VEETC would become a direct transfer for the purposes of the remaining 28 million gallons, and the producer would receive a payment from the IRS of $12.6 million (in addition to the $10 million reduction in income tax liability).

The VEETC was ultimately allowed to expire at the end of 2011 by Congress after coming under public and media attack due to its size. Initially the VEETC made uncompetitive starch ethanol producers competitive by allowing them to reduce their fuel ethanol minimum fuel selling price (MFSP) below that of gasoline in the market. The direct transfer resulted in windfall profits to ethanol producers as gasoline prices doubled between 2005 and 2008 due to higher petroleum prices, however, as the producers continued to receive the same payment from the IRS for every gallon produced even as the market value of the ethanol increased. While the large profit margins to producers that resulted from this combination caused US fuel ethanol production to rapidly increase, the cost to US taxpayers grew at

the same rate. By 2010, the US government estimated this cost to be in excess of $7 billion annually. In 2011, Congress, which by this time was focused on reducing government spending, chose to let the VEETC expire without renewal. Two similar refundable tax credits for biodiesel still exist, although their total cost is substantially lower than that of the VEETC due to the smaller scale of US biodiesel production.

13.2.3 Indirect Payments

Indirect payments are monetary transfers from one private entity to another that are required by the government. Whereas the cost burden of direct payments are distributed to taxpayers according to their tax liability, the cost burden of indirect payments falls upon a more limited group. An advantage of imposing the payment burden on a narrowly defined group is that the burden can be limited to only those entities that are affected by the industrial sector in question. Since imposing subsidy costs on taxpayers apportions them according to the taxpayer's income tax liability, under a program like the VEETC a wealthy individual relying on a bicycle for transportation carries a heavier burden of paying for the ethanol subsidy than a less wealthy individual driving a fuel-inefficient sports utility vehicle. The cost burden of indirect payments can instead be imposed on those entities with a strong connection to the subsidized product; for example, obligating petroleum refiners to pay for a biofuel subsidy results in the costs being passed down to transportation fuel consumers who have a stronger connection to the underlying purpose of the subsidy than a random taxpayer. For example, if a government's goal is to reduce its country's dependence on petroleum imports, then reducing the market price of domestic biofuels by increasing that of petroleum products imposes the costs of the program on petroleum consumers in proportion to their consumption.

One of the largest biorenewable indirect payment subsidies is a mechanism within the revised US Renewable Fuel Standard (RFS2) called the "Renewable Identification Number" (RIN). Part mandate and part indirect payment, the RFS2 mandates the consumption of specific volumes of biofuels by refiners (also known as "obligated blenders" since the refiners commonly blend the biofuels with petroleum-based fuels) on an annual basis through 2022. The RINs are attached to each gallon of biofuel following its production and identify the details of the underlying biofuel. The RINs are detached following the biofuel's blending with or use as transportation fuel by a refiner, at which point the refiner can submit them to the government to demonstrate its compliance with the mandate. To encourage the production of the biofuels, however, each RIN is also a tradable "compliance commodity." A refiner owning more RINs than are necessary to demonstrate its compliance with the RFS2 mandate for a given year can sell its excess to a refiner holding insufficient RINs, giving them a market value. Since the RINs are attached to the biofuel at the point of production, refiners must purchase both the gallon

of biofuel and the attached RIN, with the biofuel producer receiving the market value of the biofuel (equal in amount to the corresponding petroleum-based fuel on an energy content basis) in addition to the market value of the RIN. RINs therefore can be categorized as an indirect payment from refiners to biofuel producers. RIN sales are still considered to be a government subsidy despite operating as a transaction between two private entities since the government requires their purchase by refiners; were they not required by the government, the total payment from the refiner to the producer for each gallon of biofuel would not exceed its market value.

RINs are also notable in that they are a *flexible subsidy* rather than a *static subsidy*. One of the primary criticisms of the VEETC program was that it was a static subsidy that made the same payments to highly profitable producers as it did to unprofitable producers, resulting in windfall profits for the former at the expense of US taxpayers. The core value of each RIN is a function of the underlying biofuel's production cost and its market value (the latter being equal to the market value of the corresponding fossil fuel on an energy basis). This core value increases when the biofuel's production costs increase (e.g., due to higher feedstock costs) and when its market value decreases (e.g., due to lower petroleum prices). The core value decreases when the biofuel's production costs decrease (e.g., due to technological breakthroughs or improved economies of scale) and when its market value increases.

Flexible subsidies have two advantages over static subsidies. First, they ensure that producers do not generate windfall profits from the subsidy alone; RIN values are designed to fall to zero either when the biofuel's market price exceeds its production cost, thus ensuring a profit to the producer, or when the mandated volume for a given year is met. Second, flexible subsidies provide biofuel producers with an incentive to reduce their production costs over time. While the RFS2 RINs ensure that all qualifying producers initially receive enough value from the RINs to ensure profitable production, this incentive gradually decreases in value as production increases relative to the volumetric mandate. When production exceeds the mandate for a given year, the RIN core value decreases to the amount necessary to ensure the profitability of those producers with the lowest production costs. It is too low to ensure the profitability of producers with higher production costs, forcing them to either reduce their costs or cease production.

The drought that struck the US Midwest during the summer of 2012 provided a stark example of the flexible subsidy mechanism in practice. As mentioned earlier, US starch ethanol production exceeded the volumes mandated by the RFS1 and the RFS2 between 2006 and 2012. RIN values for the starch ethanol category of the RFS2 remained below $0.04/RIN through the end of 2012 even as corn prices reached historical highs due to the drought. Even though starch ethanol producers were experiencing a drastic increase in production costs even as petroleum prices remained stable, RIN values remained close to zero since starch ethanol production

exceeded the mandate, indicating that the RINs were not necessary at that point in time. In the second half of 2012 many starch ethanol producers responded to low feedstock yields by closing their facilities, causing starch ethanol production to fall below the mandated level for 2013. The starch ethanol RINs worked as designed and began to rapidly increase in value in January 2013 and quickly reached $1/RIN, a 2400% increase in value in a matter of weeks. All of this occurred without any changes to the 2007 legislation that created the RFS2 and the RINs, demonstrating the ability of flexible subsidies to automatically and effectively respond to changes in market conditions.

Another form of indirect payment is the *tariff*, which is a tax that is only levied on imports of a particular commodity or product or those from a particular foreign source. By protecting domestic production from foreign competition, tariffs permit the domestic producers in the same industry to attain greater market prices for their products. So while tariffs differ from other indirect payments in that they are not an explicit transaction from one private entity to another, the tariff beneficiary does derive higher income at the expense of both the foreign producer (via lost revenues) and the domestic consumers (via higher market values). Once common throughout the world, tariffs have declined in use due to the expansion of World Trade Organization (WTO) membership and that entity's restrictions on their use. An exception is made for tariffs on agricultural products, however, and until 2011 the United States was able to impose a substantial tariff on imports of ethanol despite its membership in the WTO. The United States continues to impose a tariff on sugarcane imports, which increases the attractiveness of corn starch as an ethanol feedstock by increasing the market price of another popular ethanol feedstock.

13.2.4 Mandates

In the biorenewables sector, mandates are government programs requiring the domestic production and/or consumption of a particular commodity or product by specific entities. (In theory consumption mandates cause their corresponding production, although the opposite is not always true.) Several countries have employed them as a means of creating markets for biorenewables by requiring their consumption, often by industries with heavy fossil fuel use such as petroleum refiners. While the early US starch ethanol industry benefited from various forms of tax credits that allowed it to compete with petroleum-derived gasoline, a major fuel ethanol market was created when the US government began requiring the blending of fuel oxygenates with gasoline by refiners to reduce certain tailpipe emissions. MTBE was initially used but eventually phased out following concerns that it was leaking from storage tanks and polluting groundwater, at which point starch ethanol was left as the primary remaining oxygenate on the market.

The US biofuel mandate was expanded by the RFS1 in 2005 and the RFS2 in 2007, although the underlying mechanism of both is the same: refiners are required

to blend predetermined volumes of biofuel with petroleum-based transportation fuels. The success of the RFS1, which just applied to starch ethanol, resulted in an increase in both the total mandated biofuel volume and the number of different biofuel categories in the RFS2. The latter mandate actually caps the starch ethanol mandate at 57 BLY while requiring the additional production of 79 BLY of so-called "advanced biofuels" by 2022. The advanced biofuels mandate is further subdivided into "cellulosic biofuel" and "biomass-based diesel" mandates, the former comprising any biofuel derived from lignocellulosic biomass and the latter consisting of biodiesel and renewable diesel produced from lipids. The cellulosic biofuel mandate is the largest of the four, reaching 61 BLY of consumption by 2022. As described in the previous section, the RFS2 mandates are combined with indirect subsidies to have the combined effect of incentivizing production and ensuring consumption.

Mandates as represented by renewable fuel standards only impact transportation fuel markets, which are responsible for just a fraction of energy market economic value and GHG emissions. A second common type of mandate is the *renewable portfolio standard* (RPS), which mandates the production of electricity from renewable sources, including biomass. Many countries and a majority of US states have individual RPS mechanisms in place. A key component of an RPS is the requirement that electricity generators in the covered state or country source a minimum percentage of their total generation from renewable sources such as hydropower, solar power, wind power, and biomass. Many RPSs are similar to the RFS2 in that a compliance certificate is associated with renewable production, passing from the renewable energy generator to the obligated party, which uses it to demonstrate its annual compliance with the mandate. Alternatively, established electricity generators can generate their own renewable electricity, eliminating the need to find a separate qualified generator.

RPSs resemble RFSs in that they are primarily market-driven mechanisms. While obligated parties are required to either purchase or generate renewable electricity for public consumption, competition allows them to choose between multiple suppliers, permitting the presence of price competition. In many countries and US states the percentage of total electricity that must be produced from renewable sources is relatively low (10–20%) in the program's early years and gradually increases over a decade or more, preventing the price shocks that can occur from a rapid and substantial transition to new and untested generation pathways. Because of the gradual natures of many RPSs, however, it will be at least a decade before their success (or failure) can be determined.

A final type of mandate that has been employed in many countries is the *feed-in tariff* (FIT). FITs differ from RFSs and RPSs in that they guarantee a price (rather than just a purchaser) for renewable electricity over periods ranging from 10 to 20 years. In Europe, for example, many countries determine the costs of production for different renewable electricity pathways and then obligate traditional electricity

generators to purchase the renewable electricity at these rates, which often exceed market electricity rates. By guaranteeing long-term future revenues for renewable electricity generators, FITs are designed to eliminate much of the uncertainty and risk from renewable electricity generation, increasing the probability that generators are able to acquire the financing necessary to construct new capacity. To prevent windfall profits, some versions of FITs include "tariff degression" or the gradual reduction of mandated tariff rates over time. Tariff degression is motivated by expected cost reductions as new renewable electricity pathways take advantage of economies of scale and increased efficiencies resulting from capacity growth.

Many European countries employing FITs have experienced substantial increases in renewable electricity generation as a percentage of total electricity generation since 2000. In some cases the FITs have been too successful, however. Spain suspended its FIT program in 2012 after new solar capacity exceeded original projections by more than 500%, imposing a substantial cost on the country's electric utilities during a time of widespread economic crisis in the European Union (EU). While the implementation of FITs can cause large increases in renewable electricity generation capacity, Spain's experience illustrates the importance of accurately estimating the minimum tariff rates necessary for each pathway to be economically feasible. Underestimating the rates results in little to no growth in capacity, while overestimating the rates imposes excessive costs on traditional electricity generators and causes regulatory uncertainty to occur as governments attempt to correct their tariff calculations.

13.3 Emission Controls

13.3.1 Carbon Prices

GHG emissions are considered to be a *negative externality* or a form of economic activity causing a negative effect that is not reflected as a cost borne by the party responsible for the activity. Air pollutants such as soot and other particulate emissions are a common example of a negative externality, as the costs of the negative human health effects caused by these emissions are carried by the general public rather than those responsible for the pollution. While GHG emissions are not as immediately visible as soot and smog, many countries legally treat them as pollutants due to concerns that excessive emissions will cause severe global climate change in the future, the costs of which will be borne by people and entities in negatively affected areas rather than by those responsible for the emissions. One method of removing negative externalities is via the imposition of a price by the government on the responsible activity. A *carbon price* imposes a monetary value on GHG emissions, generally on a mass basis (e.g., dollars per metric ton of CO_2-equivalent emissions). Under a carbon price system, emitters are required to pay the government a monetary amount based on their GHG emissions over a period

of time. Carbon prices discourage emissions by ensuring that the costs of emitting are reflected in a monetary form.

Carbon prices commonly are part of a larger *cap-and-trade* scheme. These schemes impose a cap, or ceiling, on emissions. Emitters exceeding this cap in any given year are required to purchase *carbon allowances* equal to the amount of their excess emissions. The value of the carbon allowances is determined by the carbon price. Allowances are purchased from or distributed by the government and those entities whose GHG emissions fall short of the cap can sell a number of allowances equal to the shortfall to those entities whose emissions exceed the cap. This second mechanism is the "trade" aspect of cap and trade. Over time the emissions cap is reduced, further incentivizing emission reductions by reducing the number of available carbon allowances and thus raising the carbon price, making the emissions more costly.

Cap-and-trade schemes provide multiple benefits to biorenewable pathways. Emissions caps are generally based on lifecycle emissions, allowing pathways employing sustainable biomass feedstocks to discount their smokestack or tailpipe emissions by the amount of GHGs absorbed during biomass growth (also known as biogenic carbon). Many biorenewable facilities emit a fraction of the amount of GHGs as a similarly sized fossil fuel facility on a lifecycle basis as a result. Biorenewable facilities falling under the cap thus have a greater number of carbon allowances to sell to other emitters, representing an additional source of income when the allowances are freely distributed by the government and a financial advantage relative to fossil fuel users when they are not. When the carbon price is high enough, this difference in required allowances can make biorenewable pathways economically competitive with fossil fuel pathways. Biorenewable pathways can benefit even when biorenewable facilities are not directly involved in the scheme, since the carbon price increases the production costs of fossil fuel pathways relative to biorenewable pathways, increasing the attractiveness of biorenewable investment and consumption.

An alternative method of allowing biorenewable pathways to participate in a cap-and-trade scheme is via *carbon offsets*. Biorenewable pathways not covered by the emissions cap can receive offset credits from the government for engaging in activities resulting in net carbon mitigation or sequestration, such as afforestation/reforestation, anaerobic digestion, or the production of biochar for use as a soil amendment agent. These offset credits take on a value equal to the carbon price and can be sold to GHG emitters exceeding the emissions cap, thus taking on a function that is very similar to the carbon allowances. The primary difference between allowances and offset credits is that the former are sold by entities that are covered by the cap, while the offset credits are sold by entities not otherwise included in the scheme. The offset mechanism has been employed by the European Union's Emissions Trading Scheme (ETS) as a means of reducing the atmospheric GHG concentration while providing an additional source of income for entities in

underdeveloped countries, although its initial implementation was rife with abuse and fraud. When properly designed, however, offset credits represent a means of reducing the costs of a cap-and-trade program while also reducing net global GHG emissions.

Cap-and-trade schemes are often characterized as a market-based approach to environmental regulation since the carbon price is determined in part by trading between emitters and holders of excess allowances and offset credits. While trading does affect the carbon price, the way in which the cap-and-trade scheme is designed by the government does so as well. GHG emissions, particularly those from large emitters, are closely correlated with a country's economic health; emissions tend to increase during periods of economic growth and decrease during recessions. The government is responsible for establishing the initial emissions cap level and determining the rate at which it is reduced over time. Establishing either an initial cap that is too low or a reduction rate that is too fast can cause carbon prices to be very high, effectively reducing both GHG emissions and economic growth. Alternatively, establishing either an initial cap that is too high or a reduction rate that is too slow can result in carbon prices that are so low as to be ineffective, as emitters find the purchase of allowances and offsets to be much less expensive than actual emission reductions.

The EU experienced both of these effects in implementing its ETS, first establishing a cap that was too high and then failing to reduce it quickly enough. The latter problem was compounded by the financial crisis and subsequent deep recession that afflicted the Eurozone beginning in 2008, which caused both economic growth and GHG emissions to fall far below pre-crisis projections. The ETS cap levels in the recession years were based on an expectation of economic growth, however, resulting in an oversupply of carbon allowances. The carbon price fell to very low levels in 2012 and 2013 due to this excessive supply, removing the incentive to reduce emissions via expensive equipment upgrades and adoption of economically uncompetitive renewable pathways. While the market influences the carbon price under a cap-and-trade scheme, it can only do so effectively when the government is able to accurately determine the allowance supply that will encourage the transition from fossil fuel pathways to low-carbon pathways such as biorenewables without stifling economic growth.

13.3.2 Carbon Taxes

Taxes, particularly those on income, are an integral source of government funding in developed countries. Taxes also have the effect of discouraging the activities on which they are levied by making them more expensive. Many governments levy taxes on commodities considered to be harmful to human health, such as alcohol and tobacco, in order to discourage their consumption by making them less affordable. These so-called *Pigovian taxes* are intended to correct inefficient market

outcomes by preventing the occurrence of an activity the government wishes to discourage via the imposition of high costs on it as well as provide government funding for remedial measures to counter the negative effects of the activity when it does occur (e.g., rehabilitation centers for abusers of alcohol). A *carbon tax* is an example of a Pigovian tax that is applied to carbon emissions. It is similar to a cap-and-trade scheme in that it imposes a monetary cost on the act of emitting GHGs, thereby discouraging the activity. The basic mechanism of a carbon tax can be the same as a cap-and-trade scheme in that both impose a predetermined monetary value on a particular amount of GHG emissions, either in total or above an established cap. The cost of emitting can be avoided under both systems via methods such as equipment upgrades and the adoption of renewable pathways. Despite this similarity, however, several notable differences exist between the two systems.

Carbon taxes are less flexible than cap-and-trade schemes in that they do not include a market mechanism that influences the cost of emitting. This cost is instead determined by the government prior to implementation in the form of the tax rate and must be adjusted until the optimum rate is identified. As discussed in the previous section, this is not entirely different than cap-and-trade systems in practice, as the latter require the government to determine the carbon allowance supply that is most likely to result in the optimum carbon price and update it in response to changed economic conditions. Cap-and-trade schemes do provide more flexibility on a short-term basis, however, since they allow emitters to adjust their behavior in response to changes in the availability of carbon allowances and offsets. Carbon taxes also permit less flexibility than cap-and-trade schemes in that they do not allow emitters who fall short of the cap and entities engaged in carbon mitigation and sequestration activities to directly profit via the sale of allowances and offsets to those exceeding the cap. The most that emitters can do to reduce their carbon tax burden is by reducing their net emissions. This can indirectly benefit the economic feasibility of biorenewable pathways by making them more attractive relative to fossil fuel pathways, but it does not reward net sequestration activities. While a carbon tax could impose a "negative" tax on mitigation and sequestration activities equal to the carbon tax, this would be more accurately described as a subsidy. Furthermore, this subsidy would be primarily paid by income taxpayers rather than emitters and, while the cost could be offset by the proceeds of the carbon tax, additional effort would be needed to ensure that the two remained equal.

The relative short-term inflexibility of carbon taxes notwithstanding, they are sometimes criticized for supposedly being more flexible than cap-and-trade schemes in that they do not impose a hard cap on emissions. Emissions under a cap-and-trade scheme are ultimately limited to the total availability of carbon allowances and offset credits. Under a carbon tax, emitters are only limited by their ability to pay the respective tax on all emissions, an ability that can be quite substantial for wealthy individuals and multinational corporations. In reality, however, rational actors will only ignore a carbon tax when the benefits of doing so

outweigh the costs, in which case the government can raise it to the level necessary to discourage emissions. It is unrealistic to assume that a wealthy entity would spend a fortune under a carbon tax program to emit GHGs simply for the sake of increasing the atmospheric GHG concentration. Furthermore, a government could impose a hard cap on emissions as part of a carbon tax, with the tax applying to emissions under this hard cap but above a lower soft cap.

Further Reading

Subsidies

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APPENDIX

A

Descriptions of Biorenewable Resources

Descriptions of biorenewable resources come from various sources. A good general reference is: El Bassam, N. (2010) Handbook of Bioenergy Crops: A Complete Reference to Species, Development and Applications, Earthscan LLC, Washington, DC.

Biorenewable Resources: Engineering New Products from Agriculture, Second Edition. Robert C. Brown and Tristan R. Brown.
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Sugar Crops: Sugar Beets

Taxonomic Name: *Beta vulgaris* L.

Classification: Cool season, biennial root crop

Description: Characterized by large green leaves. Plants flower during spring from autumn plantings. Seed is harvested in June and July to maximize sugar content. Average global yield of 50 Mg/ha. Specific yields can vary from 30 to 70 Mg/ha depending on climate and conditions. Tough and adaptable. Can withstand mechanical abuse, cold, heat, drought, and defoliation. Fertilized often applied to growing crops with nitrogen having greatest influence on root quality and sucrose production. Although large amounts of nitrogen are required for maximum root yield, plant should be nitrogen deficient before harvest to retard use of sucrose for growth. Major diseases caused by variety of viruses, fungi, and bacteria including curly top viral disease, leaf spot, and powdery mildew.

Natural Ecosystem: Mediterranean

Photosynthetic Pathway: C3

Cultivation History: During the Napoleonic wars of the nineteenth century, England attempted a blockade of sugarcane importation to the European continent. In response, Napoleon supported development of the sugar beet industry. Sugar beets grew from being the source of 5% of world sugar in 1840 to 50% by 1890. Since 1920 they have held steady at 40%. The first successful US production was in California in 1870.

Composition: Cellulose = 52%, Hemicellulose = 32%, Lignin = 16%

Ultimate Analysis: C = 44.5%, H = 5.9%, O = 42.8%, N = 1.84%, S = 0.13%, Cl = 0.053%

Proximate Analysis: VM = 82.5, FC = 4.1, Ash = 3.4

Higher Heating Value: 17.70 MJ/kg

Source of illustration: Author.

Sugar Crop: Sugarcane

Taxonomic Name: *Saccharum officinarum* L.

Classification: Warm-season, thick-stemmed perennial grass

Description: Tropical grass closely resembling bamboo stalks. Requires strong sunlight and abundant water. Can reach heights of 5 m. Holds many positive qualities including high sugar content, low fiber content, good ecological adaptability, and disease resistance. Nutrient requirements vary greatly among different cultivars but typically are high. Through resistance breeding most diseases no longer affect sugarcane. Insecticides may be necessary for pests such as aphids, leafhoppers, and stem borers. Maximum theoretical yields of fresh matter up to 200 Mg/ha.

Natural Ecosystem: New Guinea

Photosynthetic Pathway: C4

Cultivation History: Sugarcane was first cultivated in Polynesia. From there it spread to India. In 510 BC Persia invaded India and found "the reed which gives honey without bees." It was discovered by western Europeans as a result of the Crusades in the eleventh century. In the fifteenth century, European sugar was refined in Venice. In the same century, Columbus sailed to the Americas. It is recorded that in 1493 he took sugarcane plants to grow in the Caribbean. The climate was so advantageous for sugarcane that an industry was quickly established.

Composition: (Bagasse) Cellulose = 32–48%, Hemicellulose = 19–24%, Lignin = 23–32%

Ultimate Analysis: C = 44.80, H = 5.35, O = 39.55, N = 0.38, S = 0.01, Cl = 0.12

Proximate Analysis: VM = 73.78, FC = 14.95, Ash = 11.27

Higher Heating Value: 17.33 MJ/kg

Source of illustration: USDA-NRCS PLANTS Database / Hitchcock, A.S. (rev. A. Chase) (1950) *Manual of the Grasses of the United States*. USDA Misc. Publ. No. 200. Washington, DC.

Sugar Crop: Sweet Sorghum

Taxonomic Name: *Sorghum bicolor* (L.) Moench

Classification: Warm season, thick-stemmed annual grass

Description: Characterized by a loose, open panicle and slender upper leaves that often droop. Can grow higher than 4 m. Drought resistant and well adapted to a variety of soil types due to extensive root system. Spreads naturally through loose seed dispersion. After frost or under adverse conditions can produce toxic levels of prussic acid. Little or no response to nitrogen fertilization inputs. Very high potassium needs. Yields vary widely, depending on conditions. Can produce over 100 Mg/ha with use of irrigation.

Natural Ecosystem: Africa

Photosynthetic Pathway: C4

Cultivation History: Sorghum was likely first used as food in Ethiopia 5000 years ago. From there it spread through Africa and to India where it was first cultivated 3000 years ago. Grain varieties were brought to America with the slave trade where it was used as a hardy cover crop for livestock or grain production.

Composition: Cellulose = 27, Hemicellulose = 25, Lignin = 11

Ultimate Analysis: C = 46.8, H = 4.82, O = 39.8, N = 1.35, S = 0.07, Cl = 0.39

Proximate Analysis: 6.8% ash

Higher Heating Value: 18.322 MJ/kg

Source of illustration: USDA-NRCS PLANTS Database / Hitchcock, A.S. (rev. A. Chase) (1950) *Manual of the Grasses of the United States*. USDA Misc. Publ. No. 200. Washington, DC. *Sorghum halepense* (L.) Pers.

Starch Crop: Cassava

Taxonomic Name: *Manihot esculenta*

Classification: Perennial woody shrub often grown as an annual of the family Euphorbiaceae

Description: Dicotyledon with 1–2 m high shoot system. Consists of palmate leaves along whitish grey to brown colored stems with nodes. Root system has 5–10 tuberous roots and fibrous roots extending down to 2 m depth. Tubers are used for food, animal feed and starch-based products. Leaves are used for other proteins, vitamins and other essential elements. Vegetative propagation by stem cutting is common practice. Fourth most grown crop worldwide from Latin America, Africa to South and Southeast Asia after rice, wheat, and maize. Potential yield can be 40–90 ton/acre.

Natural Ecosystem: Lowland tropical crop which cannot withstand cold or frost. Can tolerate prolonged drought—survives by shedding leaves. Can be grown on sandy, poor soils. Yield is sensitive to drought or standing water.

Photosynthetic Pathway: Varies between C3 and C4 depending on temperature

Cultivation History: Cassava originated in Mexico, Guatemala, and northeastern Brazil. There is evidence that it was grown 5000 years ago in Columbia. It is a true cultigen, a crop unknown in the wild state.

Composition: (Root) crude protein 3.5, ether extract 0.8, crude fiber 4.2, ash 4.1, nitrogen free extract 87.4

Ultimate Analysis: Not used as boiler fuel

Proximate Analysis: Not used as boiler fuel

Higher Heating Value: 13.38 MJ/kg

Source of illustration: Author.

Starch Crop: Maize

Taxonomic Name: *Zea mays* L.

Classification: Warm season, annual grass

Description: Varies in height from 0.5 to 5 m during flowering. Maturing is 60–330 days after planting. Can grow 1–4 ears per plant, each ear containing 10–1800 kernels. Kernels can be white, yellow, red, blue, or variegated in mottled or striated patterns. Produces from 0.5 to 23.5 Mg/ha. Grown from the 40° latitude S to the 50°N. Dense, fibrous root system. Susceptible to drought, flooding, and frost. Vulnerable to many diseases and pests including various stalk and ear rots, worms, and nematodes. Diseases and pests have been overcome by chemical seed treatment, pesticides, and genetic modification.

Natural Ecosystem: Mesoamerica

Photosynthetic Pathway: C4

Cultivation History: Maize was cultivated in Mexico 4500 years before the Spanish invasion of Central America. The Spanish brought maize back to Europe. Scientists have since developed different types of maize that can grow in many different climates throughout the world.

Composition: (Stover) Cellulose = 35%, Hemicellulose = 28%, Lignin = 16–21% (Grain) Starch = 72, Protein = 10, Oil = 5, Fiber = 13

Ultimate Analysis: (Cobs) C = 46.58, H = 5.87, O = 45.46, N = 0.47, S = 0.01, Cl = 0.21 (Stover) C = 43.65, H = 5.56, O = 43.31, N = 0.61, S = 0.01, Cl = 0.60

Proximate Analysis: (Cobs) VM = 80.1, FC = 18.54, Ash = 1.36 (Stover) VM = 75.17, FC = 19.25, Ash = 5.58

Higher Heating Value: (Cobs) 18.77 MJ/kg; (Stover) 17.65 MJ/kg

Source of illustration: USDA-NRCS PLANTS Database / Britton, N.L. and Brown, A. (1913) *Illustrated Flora of the Northern States and Canada,* Vol. 1: 599.

Inulin Crop: Jerusalem Artichoke

Taxonomic Name: *Helianthus tuberosus* L.

Classification: Perennial herb often cultivated as an annual

Description: Stems are 1–3 m tall with vegetation similar to a sunflower but perennating from stem tubers. Both crop forage and tubers can be harvested. Production costs and techniques are similar to those for potatoes. Typical yields under normal conditions are 20 Mg/ha. Weed control is not a large issue as the plant shades the ground as it matures.

Natural Ecosystem: Native to North America. Has been introduced and become naturalized in all temperate regions in the Northern and Southern Hemispheres.

Photosynthetic Pathway: C3

Cultivation History: Jerusalem artichoke is grown primarily for the tubers that can be eaten cooked or raw. It was largely cultivated in the northeast United States until the mid-eighteenth century when it was replaced by the potato. Both its foliage and the tuber can be used as energy crops. The tuber contains large amounts of the carbohydrate inulin that can be used in the production of alcohols. It is a high yield crop that makes it attractive for production of ethanol.

Composition: Water 80%; Remainder: Inulin 65%, Protein 15%, Fat 1%, Fiber 4%, and Ash 5%

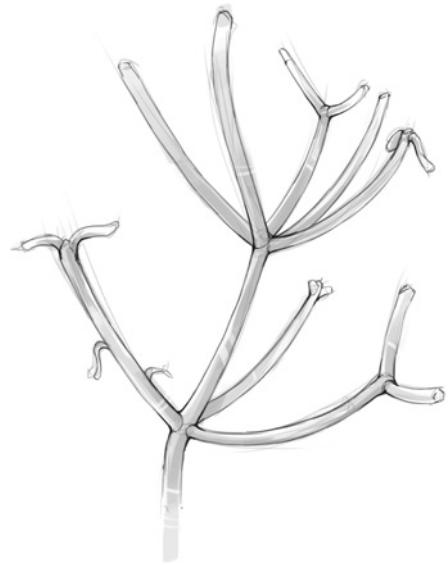
Ultimate Analysis: Not used as boiler fuel

Proximate Analysis: Not used as boiler fuel

Higher Heating Value: Not used as boiler fuel

Source of illustration: USDA-NRCS PLANTS Database / Britton, N.L. and Brown, A. (1913) *Illustrated Flora of the Northern States and Canada*, Vol. 3: 486.

Oleaginous Crop: Aveloz



Taxonomic Name: *Euphorbia tirucalli* L.

Classification: Dioecious, succulent, cactus-like milky tree

Description: A perennial with many names including petroleum plant, mole plant, caper spurge, pencil tree, milk bush, and finger tree. Grows with single or multiple trunks that support a tangle of light green, pencil-thick, branches with little sign of leaves. Can reach heights up to 10 m with a 2–3 m spread. Main trunk and branches are woody and brownish. It produces a corrosive white latex sap.

Natural Ecosystem: Indigenous to tropical eastern and southern Africa

Photosynthetic Pathway: Crassulacean acid metabolism (CAM)

Cultivation History: Aveloz was introduced from Africa as a garden plant, but is now naturalized in tropical areas and rainforests in South Africa, Amazon, and Madagascar. Its use as a tribal and herbal medication dates back thousands of years to areas in Brazil, Africa, Malaysia, India, and Peru. In the 1970s, aveloz was touted as a cure for cancer but it was subsequently shown to be an immune system suppressant. The interest for the aveloz as a biorenewable resource came from 1976, when the Nobel Laureate Melvin Calvin suggested that the plant could be the "petroleum plant" due to its production of a hydrocarbon substance. Aveloz has been studied by Petrobras, the Brazilian state petroleum company, as a refinery feedstock.

Composition: (Plant) Hydrocarbon = 5.92%, Sugar = 10.21%; (Seed) Oil = 48%

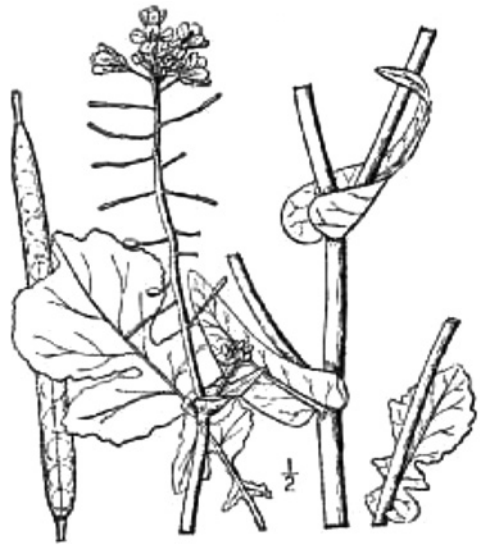
Ultimate Analysis: Not available

Proximate Analysis: Not available

Higher Heating Value: (Oil) 44 MJ/kg; (Hydrocarbon) 42 MJ/kg

Source of illustration: Author.

Oleaginous Crop: Canola



Taxonomic Name: *Brassica napus* L.

Classification: Cool season, bright yellow flowering member of the mustard family

Description: Annual with low drought tolerance. Mature plants are 1.5 m tall, non-nitrogen fixing, and propagated by seed. Non-native to the United States.

Natural Ecosystem: Cool extremes of temperate zones

Photosynthetic Pathway: C3

Cultivation History: Canola refers to cultivars of oilseed rape developed in Canada. It was first grown as an emergency war measure on a few acres in 1942. It is bred for low levels of erucic acid. It is widely used for cooking oil, salad oil, and margarine. Canola contains the lowest saturated fat content of all major edible vegetable oils.

Composition: (Seeds) Moisture = 8.5%, Protein = 20.4%, Lipid = 42.4%

Ultimate Analysis: C = 52.2%, H = 8.06%, O = 35.8%, N = 3.91%, Ash = 5.50%

Proximate Analysis: VM = 82.6%, FC = 7.90%, Ash = 5.5%

Higher Heating Value: 28.36 MJ/kg

Source of illustration: USDA-NRCS PLANTS Database / Britton, N.L. and Brown, A. (1913) *Illustrated Flora of the Northern States and Canada*, Vol. 2: 193.

Oleaginous Crop: Chinese Tallow Tree

Taxonomic Name: *Sapium sebiferum*

Classification: Tropical hardwood

Description: Deciduous tree that can reach 16 m. Matures in 3–5 years. Can be propagated by coppicing.

Natural Ecosystem: Eastern Asia

Photosynthetic Pathway: C3

Cultivation History: The Chinese tallow tree has been cultivated in China for about 1500 years as a seed-oil crop. It has since been established in the outer coastal plains of North and South Carolina, south to Florida, and west to eastern Texas. The wood of the tree can be used as boiler fuel while the seed yields both oil and high-protein meal. The oil is considered superior to linseed oil in its drying and polymerizing properties. The meal can be processed into refined flour suitable for human consumption.

Composition: (Fruit) Fatty seed coat = 27–33%, Shell = 36–41%, Kernel = 29–35%. (Outer seed coat) Fat = 55–78%. (Kernel) Fat = 53–64%.

Ultimate Analysis: Not available

Proximate Analysis: Not available

Higher Heating Value: (Wood) 16.8–18.27 MJ/kg

Source of illustration: Author.

Oleaginous Crop: Jojoba

Taxonomic Name: *Simmondsia chinensis* (Link) Schneid

Classification: Perennial, deciduous, evergreen shrub, or small tree

Description: Shrub that reaches 4.5 m in height with flat, gray-green, leathery leaves. Deep and extensive root system. Well adapted to withstand desert heat and aridity. Can live under diverse environmental conditions. May live for up to 200 years. During summer, green fruit dries, outer skin shrivels, and peels back, exposing a wrinkled, brown, soft-skinned nut, the size of a small olive. Nuts contain a vegetable oil that is clear and odorless but feels less oily than traditional edible oils. Half the weight of the nut is oil. The oil is a polyunsaturated liquid wax whose only other known source has been the sperm whale. Seeds yield methyl ester instead of the triglycerides of most seeds' oils. The ester does not turn rancid.

Natural Ecosystem: Hot, arid and semiarid regions of the southwestern United States (Sonoran Desert)

Photosynthetic Pathway: C3

Cultivation History: Native Americans extracted the oil from jojoba seeds to treat sores and wounds centuries ago. Jojoba cultivation began in the early 1970s. Average yield of commercial jojoba plantations is approximately 340 kg/ha.

Composition: (Seed) Water = 4.45%, Protein = 15%, Fat = 52%, Carbohydrate = 26.85%, Fiber = 3.85%, Ash = 1.5%

Ultimate Analysis: C = 81.8%, H = 5.2%, O = 13%

Proximate Analysis: Not available

Higher Heating Value: (Oil) 42.761 MJ/kg

Source of illustration: Author.

Oleaginous Crop: Rapeseed

Taxonomic Name: *Brassica napus* L.

Classification: Warm season or cold season, annual or biennial oil plant depending on cultivar

Description: Composed of a deep taproot and a rosette of blue-green leaves with 7–10 lateral shoots. Gold-yellow flowered racemes are located on the ends of the branched stems. Contains approximately 120 long, slender seed pods per plant with 18–20 seeds per pod (2000–3000 seeds per plant). Germinates quickly. Small, round, black seeds. Crop success very sensitive to water levels. Seed yield can reach 3 Mg/ha with 10–12 Mg/ha dry matter straw yield. Common problem weeds include chickweed, foxtail grass, chamomile, and reappearing wheat. Insecticides may be required for pests such as fleas, lice, snails, beetles, and weevils. Fungicide applications may be necessary. Reaches heights of up to 1.5 m. Yields approximately 40% oil.

Natural Ecosystem: Mediterranean region

Photosynthetic Pathway: C3

Cultivation History: Rapeseed remnants have been found in digs from Bronze Age establishments. Large-scale cultivation has been established as far back as the thirteenth century. Rapeseed began to spread to western Europe, Canada, China, India, and the United States following World War II. It is the third largest oil-producing seed behind soybeans and palm.

Composition: (Straw) Holocellulose = 75.43, Lignin = 19.34, Ash = 5.23

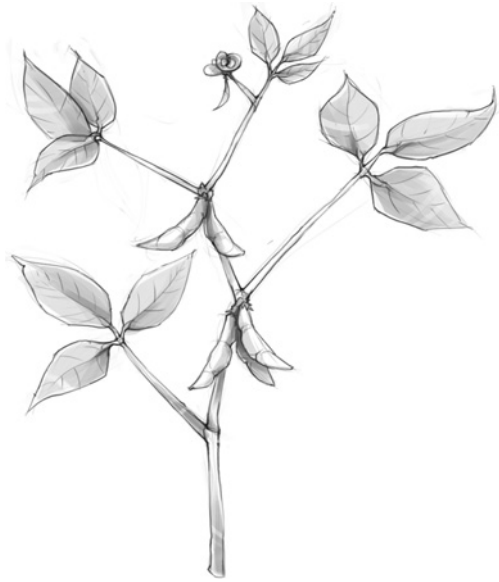
Ultimate Analysis: (Straw) C = 45.2%, H = 5.15%, O = 42.9%, S = 0.14%, N = 0.75%

Proximate Analysis: (Straw and Stalk) VM = 75.6%, FC = 18.6%, Ash = 5.87%

Higher Heating Value: (Straw) 17.64 MJ/kg; (Oil) 39.7 MJ/kg

Source of illustration: Author.

Oleaginous Crop: Soybean



Taxonomic Name: *Glycine max* (L.) Merr.

Classification: Annual, cool season legume. Can be grown as warm-season plant in tropical areas

Description: Rapid growing nitrogen producing plant. Grows to a height up to 80 cm. Entire plant covered in hair. Produces a main root with smaller roots branching from it which possess numerous nodules. Bacteria *Bradyrhizobium japonicum* develops in the roots and is responsible for free nitrogen fixation. Leaves usually consist of three leaflets. Numerous small purple or white flowers are found in compact racemes in the leaf axils. Fruit develops in the form of pods with 2–3 seeds usually being found in each pod. Drought strongly affects crop yield. Common diseases include leaf spot, stem canker, and soybean mosaic virus. Insecticides may be necessary for pests such as soya bean moth, Japanese beetle, and nematodes. Yields of up to 3.6 Mg/ha.

Natural Ecosystem: China

Photosynthetic Pathway: C3

Cultivation History: The soybean was domesticated in China over 3000 years ago. The first soybeans arrived in America in the early 1800s as ballast aboard a ship, but soybeans were not harvested in America until 1879 when farmers began to plant soybeans as forage for their livestock. The plants flourished in the hot, humid summer of northeastern North Carolina. In 1904, G.W. Carver discovered that soybeans were a valuable source of protein and oil. Soybeans have been recently genetically modified to produce oil for a number of products including biodiesel fuel, printing inks, paints, soaps, shampoos, and disinfectants.

Composition: (Seed) Protein = 40%, Lipid = 20%, Carbohydrates = 35%, Ash = 4.9%

Ultimate Analysis: Not available

Proximate Analysis: Not available

Higher Heating Value: (Oil) 39.6 MJ/kg

Source of illustration: Author.

Oleaginous Crop: Sunflower

Taxonomic Name: *Helianthus annuus* L.

Classification: Warm season, annual broadleaf plant

Description: Erect, broadleaf plant. Head is not a single flower but is made up of 1000–2000 individual flowers joined at a common receptacle. Most varieties have rough/hairy oval to heart shaped leaves. Leaves will follow the sun's rays, increasing light interception and photosynthesis. Not highly drought tolerant, but often produces satisfactory results when other crops are damaged during drought. Will grow in a wide range of soil types from sands to clays. Yield increases from N fertilizer rates up to 196 kg/ha have been observed. Heights reaching up to 3.5 m. Head can grow up to 40 cm in diameter with spirally arranged yellow flowers. Strong taproot up to 3 m deep.

Natural Ecosystem: North America

Photosynthetic Pathway: C3

Cultivation History: The wild sunflower was domesticated around 3000 BC for food production. It was taken to Europe around 1500, where improved varieties were developed. It became very popular as a cultivated plant in the eighteenth century when Russians started using it for its oil. The sunflower returned to the United States in the end of the nineteenth century. US acreage increased during the 1970s due to strong European demand for sunflower oil. It was hybridized in the mid-1970s, providing higher yield, oil enhancement, and disease resistance.

Composition: (Shell) Cellulose = 48.4%, Hemicellulose = 34.6%, Lignin = 17%

Ultimate Analysis: C = 44.2, H = 4.6, N = 0.7, S = 0.1, O = 50.4

Proximate Analysis: FC = 13.3, VM = 6.2, Ash = 10.5

Higher Heating Value: Shell (18.0 MJ/kg); Seed (15.6 MJ/kg); Oil (39.6 MJ/kg)

Source of illustration: Author.

Herbaceous Crop: Big Bluestem

Taxonomic Name: *Andropogon gerardii* Vitman

Classification: Warm season perennial grass

Description: A native prairie grass that grows in clumps, forms a dense sod and can grow to 2.4 m tall. The root system can extend down to 3.7 m making it very drought resistant. It spreads by seed or by rhizomes. Unlike the hollow stems of most grasses, the stems are solid or pithy. The leaves and stem nodes have a bluish cast. The seed heads often occur as three branches giving rise to its common name "turkey foot."

Natural Ecosystem: Its primary natural ecosystem is the North American tallgrass prairie biome, which once extended from southern Manitoba to Texas and from eastern Nebraska to Indiana.

Photosynthetic Pathway: C4

History: The dominate grass of the tallgrass prairies. A higher stem to leaf ratio makes it more attractive than switchgrass as a potential fiber crop.

Composition: Cellulose = 34%, Hemicellulose = 24%, Lignin = 18%

Ultimate Analysis: C = 47.4%, H = 5.75%, O = 42.3%, N = 0.74%, S = 0.08%

Proximate Analysis: VM = 81.4%, FC = 15%, Ash = 3.6%

Higher Heating Value: 18.64 MJ/kg

Source of illustration: USDA-NRCS PLANT Database / Hitchcock, A.S. (rev. A. Chase) (1950) *Manual of the Grasses of the United States.* USDA Misc. Publ. No. 200. Washington, DC.

Herbaceous Crop: Kenaf

Taxonomic Name: *Hibiscus cannabinus* L.

Classification: Warm season, annual

Description: Herbaceous plant with a single, straight, unbranched stem. Can grow to heights of about 4–6 m with a 25–50 mm diameter stem. Exhibits rapid growth, reaching full height in 5–7 months. Yields as high as 24 Mg/ha can be obtained with 120 lb of N2 application. Very sensitive to cold. Requires frequent irrigation in sandy soils. Cannot tolerate waterlogged soils.

Natural Ecosystem: Africa

Photosynthetic Pathway: C4

Cultivation History: Kenaf has grown for thousands of years in Africa and was introduced to southern Asia in early 1900. In 1980, kenaf was introduced and researched in the United States. It has the potential to be a renewable source of industrial fiber (mostly for pulp and paper industry) in developed economies.

Composition: Cross and bevan cellulose 47–52%, alpha cellulose 31–39%, lignin 7.5–9.5%, pentosans 16–23%, ash 2–5.5% (bast) alpha cellulose 34%, lignin 17.5%, pentosans 19.3%, ash 2.5% (core)

Ultimate Analysis: Not available

Proximate Analysis: Not available

Higher Heating Value: Not available

Source of illustration: Author.

Herbaceous Crop: Miscanthus

Taxonomic Name: *Miscanthus* × *giganteus*

Classification: Cool season, thick-stemmed perennial grass

Description: Deep-rooted (at least 1 m penetration) grass hybrid with heights usually ranging between 2 and 3 m that can attain heights as large as 3.5 m. Lifetime of at least 10–15 years. Sometimes known as "elephant grass." Naturally occurring sterile species hybrid of the *sinensis* and *sacchariflorus* species. Low nutrient requirements allow growth in a wide variety of soils. Will tolerate dry conditions, but at the cost of yield. Under normal conditions offers high yields ranging from 8 to 15 Mg/ha. Can be harvested annually with a sugarcane harvester.

Natural Ecosystem: Southeast Asia

Photosynthetic Pathway: C4

Cultivation History: While originally from Japan, miscanthus has been propagated by harvesting rhizomes from existing stands and replanting them elsewhere. The sterile nature of this hybrid eliminates the threat of a non-native invasion. Miscanthus is a genus of 14 species widely grown as an ornamental plant because of its attractive inflorescences. Genotypes developed for biomass are selected for delayed flowering and for infertile hybrids to avoid it becoming a weed. *Miscanthus* × *giganteus is* the cross most commonly used for biomass production.

Composition: Cellulose = 46%, Hemicellulose = 29%, Lignin = 15%

Ultimate Analysis: C = 45.7, H = 5.70, O = 41.1, N = 0.46, S = 0.11

Proximate Analysis: VM = 69.7, FC = 27.7, Ash = 2.60

Higher Heating Value: 17.1 MJ/kg

Source of illustration: USDA-NRCS PLANTS Database / Hitchcock, A.S. (rev. A. Chase) (1950) *Manual of the Grasses of the United States*. USDA Misc. Publ. No. 200. Washington, DC.

Herbaceous Crop: Switchgrass

Taxonomic Name: *Panicum virgatum* L.

Classification: Warm season, thin-stemmed perennial grass

Description: Deep-rooted bunch grass that grows as tall as 2.5 m. Natural prairie grass that is drought resistant. Demand for nitrogen is low due to deep rooting and storage of nutrients in rhizomes. Once established, need for pesticides are low. High yielding, as much as 10 Mg/ha. Can be distinguished from other warm-season grasses by a white patch of hair at the point where the leaf attaches to the stem. Stem is round and usually has a reddish tint.

Natural Ecosystem: North to Central America

Photosynthetic Pathway: C4

Cultivation History: Switchgrass was one of the main species forming the North American grass prairies before the coming of the plow. It is valued as a soil stabilization plant, and is used as a windbreak in crop fields. It was selected by the US DOE as an early candidate among prospective dedicated energy crops and has been used in demonstrations of biomass power.

Composition: Cellulose = 43%, Hemicellulose = 36%, Lignin = 22%

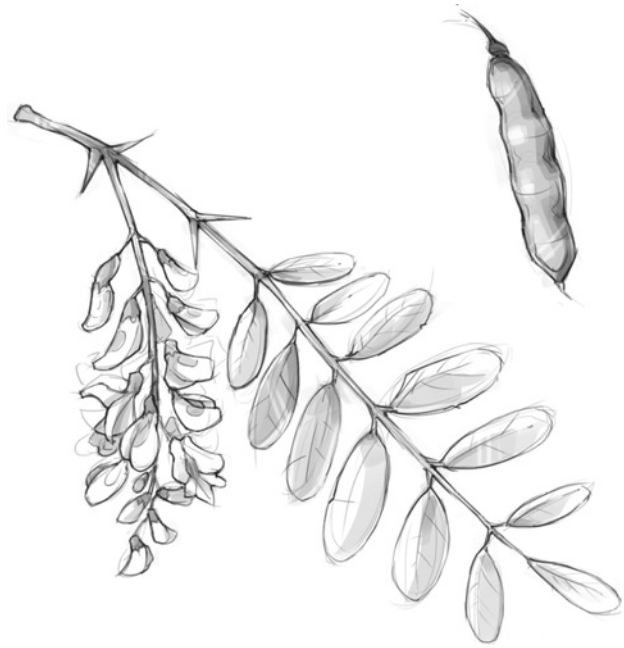
Ultimate Analysis: C = 47.2, H = 5.79, O = 41.2, N = 0.62, S = 0.10

Proximate Analysis: VM = 80.3, FC = 14.6, Ash = 5.1

Higher Heating Value: 18.4 MJ/kg

Source of illustration: USDA-NRCS PLANTS Database / Hitchcock, A.S. (rev. A. Chase) (1950) *Manual of the Grasses of the United States*. USDA Misc. Publ. No. 200. Washington, DC.

Woody Crop: Black Locust



Taxonomic Name: *Robinia pseudoacacia* L.

Classification: Perennial, leguminous hardwood

Description: Rapid growing, nitrogen-fixing tree that tolerates low fertility sites and yields 6–14 Mg/ha. When mature, this perennial can reach 35 m in height and 1 m in diameter. It regenerates from root sprouts or coppice, but is intolerant to shade. Attributes include wide climatic adaptation, resistance to drought stress and decay fungi, and high genetic variation. Its dense (690 kg/m^3) wood is extremely durable, though plagued by stem borer, *Megacyllene robiniae*.

Natural Ecosystem: Cool, temperate regions of eastern United States

Photosynthetic Pathway: C3

Cultivation History: In early US history, houses were built on posts of black locust. Later it was used for erosion control, land reclamation after strip-mining, and timber production on abandoned farmlands. Potential includes use as a fiber or energy crop. Though native to eastern United States, it is now being developed and cultivated throughout the world.

Composition: Cellulose = 45%, Hemicellulose = 19%, Lignin = 29%

Ultimate Analysis: C = 50.7, H = 5.71, O = 41.9, N = 0.57, S = 0.01

Proximate Analysis: VM = 80.9%, FC = 18.3%, Ash = 0.80%

Higher Heating Value: 19.87 MJ/kg

Source of illustration: Author.

Woody Biomass: Eucalyptus

Taxonomic Name: *Eucalyptus globulus* Labill

Classification: Mytaceae, perennial fast growing tree

Description: Rapid growing tree, up to 25 m in its first 20 years. Actively grows in all but summer season. Tree can grow in a variety of soil types in areas with mild weather conditions and high moisture content. Cannot tolerate cold, frost, drought, or harsh winds. Secretes fragrant, sticky gum containing antibacterial properties, increasing pest resistance. Deters growth of non-eucalyptus plants. Prefers to grow in dense stands. Mean annual yield for California estimated at 270 ft^3/acre. Planting density at over 10 000 plants/ha.

Natural Ecosystem: Native to Australia, introduced to California and other countries

Photosynthetic Pathway: C3

Cultivation History: The Tasmanian blue gum was first discovered and described in 1792 in Tasmania. It was introduced to California in 1856. It is one of the world's most valuable windbreak trees because of its wind firmness and the unpalatable nature of its seedlings to grazing animals. It is used as fuel wood in many countries and leaves little ash. Its bark is often used for pulpwood. Essential oils can be extracted from its leaves, and honey can be produced from its flowers. It has potential as industrial fuel wood.

Composition: Glucose 59.5%, Xylose 17.8%, Galactose 5.4%, Mannose 2.8%, Rhamnose 0.8%

Ultimate Analysis: C = 50.4, H = 6.0, N = 0.17, S = 0.08, Cl = 0.02, O = 43.3

Proximate Analysis: VM = 81.42, FC = 17.82, Ash = 0.76

Higher Heating Value: 19.1 MJ/kg

Source of illustration: Author.

Woody Crop: Hybrid Poplar

Taxonomic Name: *Populus* × *canadensis* Moench 'I-45/51'

(Populus deltoides × *Populus nigra)*

Classification: Hardwood

Description: Grows very rapidly, reaching a height of 6.5 m in 7–8 years. Crown shape varies with different clones, but generally is very loose, providing little winter protection. Short lived under arid conditions (20–25 years) while under moist conditions may reach 20–24 m and survive 50–60 years. Roots are shallow and may spread 15–20 m.

Natural Ecosystem: Widely distributed in Northern Hemisphere

Photosynthetic Pathway: C3

Cultivation History: Early French explorers in North America brought home eastern cottonwood (*Populus deltoides*), which crossed naturally with poplars in Europe (*P. nigra*). Hand-pollinated poplar hybrids were first produced in Britain in 1912, and many European countries established plantations after the World War II, in response to shortages of timber. Since 1979, the task of improving hybrid poplar as an energy crop has been conducted in the United States. Research has focused on reducing costs by improving yields, increasing pest and disease resistance, and developing efficient management systems.

Composition: Cellulose = 39%, Hemicellulose = 17%, Lignin = 25%

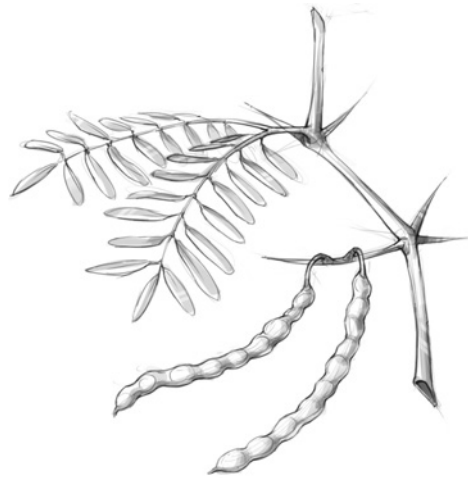
Ultimate Analysis: C = 49.75, H = 5.52, O = 42.42, N = 0.52, S = 0.03

Proximate Analysis: VM = 78.7, FC = 19.96, Ash = 2.03

Higher Heating Value: 8384 BTU/lb

Source of illustration: USDA Natural Resource and Conservation Service PLANTS Database. *Populus nigra* L. http://plants.usda.gov/

Woody Crop: Mesquite



Taxonomic Name: *Prosopis glandulosa* Torr.

Classification: Small to medium sized hardwood tree

Description: Commonly called honey mesquite. Tall shrub or tree growing 3–9 m in height. Foliage is deciduous, and wood is very dense at above 0.7 SG. Propagates aggressively through rhizomes, and also deposits nitrogen in the ground (legume). Tolerates annual precipitation as low as 30 cm and as high as 200 cm and annual temperatures of 18–21°C. Ranked in the "unfailing" class of perennial crops because of the ability to produce fruit independent of annual precipitation trends. Root system has been observed to reach depths of up to 50 m, allowing for high drought resistance.

Natural Ecosystem: Grows in southern North America, central and southern South America, sub-Saharan Africa, and regions of the Middle East. Natural ecosystem is semi-arid to arid dessert.

Photosynthetic Pathway: C3

Cultivation History: Mesquite was a key resource of indigenous people due to its drought resistance, providing food, alcohol drink, fuel, medicine, and fertilizer. In more recent years it has been considered more a nuisance, but is still used for firewood, fence posts, and woodworking.

Composition: Cellulose = 42%, Hemicellulose = 38%, Lignin = 18%

Ultimate Analysis: Not available

Proximate Analysis: Not available

Higher Heating Value: 20 MJ/kg

Source of illustration: Author.

Woody Crop: Willow

Taxonomic Name: *Salix* sp.

Classification: Hardwood

Description: Most are compact shrubs with numerous thick branches and grow to heights between 0.3 and 4 m. Some are true trees that reach 15–20 m (*S. fragilis* and *S. alba*). Some species build leaves before blossoms in spring. Shrubs normally have extensive root system. *S. viminalis* (L.) and *S. dasyclados* (Wimm.) are cultivated on biomass plantations for use as energy sources. Very dependent on water availability. Weed control necessary during the first year of establishment. Average application of 60–80 kg/ha N, 10 kg/ha P, and 35 kg/ha K suitable after first year. May be attacked by numerous insects but none cause serious problems. Diseases are more of problem but can be controlled. Considerable damage may be caused by mice and deer during establishment phase. Can produce first yield in three years.

Natural Ecosystem: Common across many continents and grows in many climates

Photosynthetic Pathway: C3

Cultivation History: Willow is a prominent candidate for plantations of short-rotation woody crops in northern climates, especially the basket willow (*Salix viminalis*). Several large field trials have been performed in the state of New York and northern Europe. Grown in short rotations (3–5 years) and harvested when 5–7 m in height. Regenerates from stump and roots, allowing 6–10 rotations before replanting.

Composition:

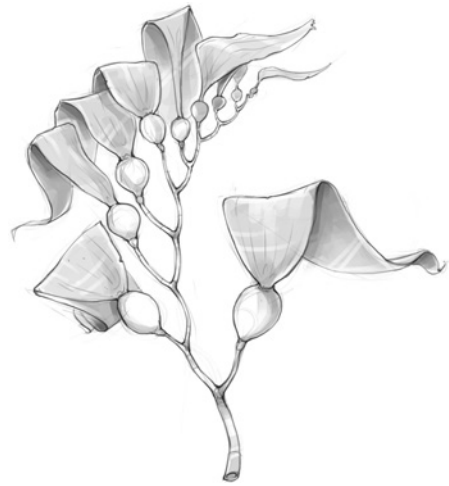
Ultimate Analysis: C = 47.7%, H = 5.72%, O = 46.2%, N = 0.43%, S = 0.03%, Cl = 0.01%

Proximate Analysis: FC = 12.4%, VM = 76.5%, Ash = 0.85%, Moisture = 10.2%

Higher Heating Value: 19.2 MJ/kg

Source of illustration: Britton, N.L. and Brown, A. (1913) *An Illustrated Flora of the Northern United States, Canada and the British Possessions*, 3 vols. New York: Charles Scribner's Sons.

Aquatic Species: Giant Brown Kelp



Taxonomic Name: *Macrocystis pyrifera*

Classification: Eukaryota, cold season, perennial kelp

Description: May reach 45.7 m long and grow in waters 6–20 m deep. Largest of the Pacific kelps. Can grow more than 45 cm per day. Usually grows in beds called forests. Buoyed up by many small, gas-filled bulbs. Attaches to rocks on the ocean floor by means of a large holdfast.

Natural Ecosystem: Alaska to Baja California

Photosynthetic Pathway: C3

Cultivation History: Giant brown kelp was originally used as a fertilizer, then later in the manufacture of gunpowder and as animal feed. Much of today's harvest is used to produce chemicals for the manufacture of medicines, plastics, beauty aids, paper, clothing, and processed foods.

Composition: 5–25% mannitol, 12–20% algin, 56–82% cellulose

Ultimate Analysis: C = 27.8%, H = 3.77%, O = 23.7%, N = 4.6%, S = 1.1%

Proximate Analysis: 57.9% volatiles, 42.1% ash

Higher Heating Value: 10.75 MJ/kg

Source of illustration: Author.

Aquatic Species: Common Water Hyacinth

Taxonomic Name: *Eichhornia crassipes*

Classification: Tropical/sub-tropical obligate flowering perennial

Description: Floating, aquatic plant. Height ranges from a few centimeters to nearly a meter tall. Long feathery roots. Rounded, leathery leaves attached to bulbous spongy petioles that are sometimes inflated for buoyancy. Multiplies quickly by runners (stolon) from primary plant. Can produce up to 248 secondary plants in 90 days under ideal conditions. Linked plants from thick mats. Can bloom and produce seeds but runners are primary method for multiplication.

Natural Ecosystem: Located in freshwater rivers, ponds, streams, ditches around the world in temperate climates.

Photosynthetic Pathway: C3

Cultivation History: The water hyacinth originated in Latin America. It is believed it was introduced to Africa in the nineteenth century as a pond decoration. It was reportedly brought to the United States in 1884 at an exposition in New Orleans. It is considered one of the most aggressive plants in the world with more than 50 countries listing it as a weed.

Composition: Cellulose = 29.3%, Hemicellulose = 33.2%, Lignin = 4.79%, Other = 4.79%

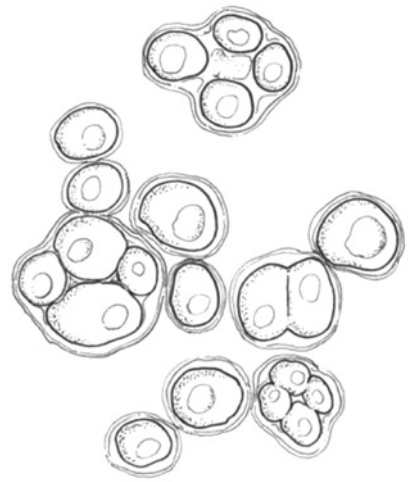
Ultimate Analysis: C = 41.1%, H = 5.3%, O = 51.2%, N = 1.96%, S = 0.41%

Proximate Analysis: Not available

Higher Heating Value: 16.02 MJ/kg

Source of illustration: Author.

Aquatic Species: Microalgae



Taxonomic Name: Various (thousands of strains have been analyzed)

Classification: Nonvascular flora, Kingdom Protist, Phyla Chlorophyta

Description: Found in both freshwater and marine systems. Depending on species, size ranges from a few to several hundred micrometers. Can exist individually, although many harvestable species grow in chains or groups. Can be phototrophic, heterotrophic, or mixotrophic. Yield a variety of carotenoids, antioxidants, enzymes, polymers, and lipids. Lipids yield estimated to be as high as 15 000 gallons/acre/year, depending on species and cultivation conditions.

Natural Ecosystem: Freshwater and marine systems. Prefer warmer climes, although some species can grow in closed bioreactors.

Photosynthetic Pathway: C3

Cultivation History: Microalgae naturally occurs in aquatic systems. Initially grown in small-scale raceway pond systems located in California and Hawaii by the US government in the 1980s. Small-scale raceway ponds and closed bioreactors now exist in several locations globally, while larger ponds are under construction in the southwest United States and Mexico.

Composition: Depends on species, but up to 50% oil, remainder protein, carbohydrate, ash

Ultimate Analysis: C = 43%, H = 7%, N = 6%, O = 28%

Proximate Analysis: 67% volatiles, 12% fixed carbon, 16% ash

Higher Heating Value: 17 MJ/kg

Source of illustration: Brown, R. and Brown, T. (2012) *Why Are We Producing Biofuels?* Brownia, LLC.

APPENDIX

B

Conversion Factors

Area

1 hectare (ha) = 10,000 m^2
1 hectare (ha) = 2.471 acres
1 acre = 43,560 ft^2

Volume

1 liter (L) = 10^{-3} m^3
1 liter (L) = 0.2642 gallons
1 cubic meter (m^3) = 35.31 cubic feet
1 cubic meter = 264.2 gallons
1 barrel (bbl) = 42 gallons
1 bushel = 1.244 ft^3

1 bushel corn = 25.4 kg
1 bushel wheat = 27.2 kg
1 bushel soybean = 27.2 kg

Weight

1 kg = 2.205 lb
1 ton (metric) = 1000 kg
1 ton (English) = 2000 lb
1 ton (metric) = 1.1 ton (English)
1 ton per day (tpd) = 0.015 kg per sec (kg/s)

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Energy

1 joule (J) = 1 kg m^2/s^2
1 kilojoule (kJ) = 10^3 J
1 megajoule (MJ) = 10^6 J
1 gigajoule (GJ) = 10^9 J
1 terajoule (TJ) = 10^{12} J
1 petajoule (PJ) = 10^{15} J
1 exajoule (EJ) = 10^{18} J

1 British thermal unit (Btu) = 1054 J
1 thousand Btu (MBtu) = 10^3 Btu
1 million Btu (MMBt) = 10^6 Btu
1 quadrillion Btu (quad) = 10^{15} Btu
1 quad = 1054×10^{15} J (approximately 1 EJ)

1 toe (metric ton oil equivalent)
= 7.4 barrels of crude oil in primary energy
= 7.8 barrels in total final consumption
= 1270 m^3 of natural gas
= 2.3 metric ton of coal

Power

1 kilowatt (kW) = 1 kJ/s
1 megawatt (MW) = 1000 kW
1 MW = 3.415 MMBtu/hr
1 horsepower (hp) = 2546 Btu/hr
1 horsepower (hp) = 550 ft-lb/s

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